Iodine Clathrated : A Solid-State Analog of the Iodine-Starch Complex

Pan, Fangfang; Chen, Yingchun; Li, Siyu; Jiang, Minzhi; Rissanen, Kari

Year: 2019

Version: Accepted version (Final draft)

Copyright: © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Rights: In Copyright

Rights url: http://rightsstatements.org/page/InC/1.0/?language=en

Please cite the original version:

Accepted Article

Title: Iodine Clathrated: A Solid-State Analog of the Iodine-Starch Complex

Authors: Kari Rissanen, Fangfang Pan, Yingchun Chen, Siyu Li, and Minzhi Jiang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201901734

Link to VoR: http://dx.doi.org/10.1002/chem.201901734
Iodine Clathrated: A Solid-State Analog of the Iodine-Starch Complex


Abstract: Co-crystallizing iodine with a simple dicaticonic salt (1,8-diammoniumoctane chloride) results in the clathration of the iodine (I$_2$) molecules inside trigonal and hexagonal channels of the crystal lattice with 72 wt% overall I$_2$ loading. The I$_2$ inside the bigger trigonal channel forms a I-•••I-I-•••I-I halogen-bonded infinite helical chain, while the I$_2$ in the smaller hexagonal channel is disordered. In both channels the I$_2$ interaction with the channel wall happens through I-•••Cl halogen bonds. The helical channels in the crystal lattice are constructed via the strong charge-assisted H$_2$N$^+$-H$^+$-Cl$^-$ hydrogen bonds between the dications and the chloride anions. The structure shows a marked similarity with the well-known starch-I$_2$ system, and thus may provide insight for the yet unresolved structure of the I$_2$ in the helical starch channel.

Clathration (entrapment of a guest) is a fundamental process in supramolecular chemistry, whether being molecular, viz. host-guest chemistry, or solid-state phenomenon, viz. lattice clathration.[9] Iconic lattice clathrate examples are the chlorine[9] methane and natural gas[9] clathrates. A specific form of clathration is iodine-starch complex, which is considered to be a clathrate of polyiodide and carbohydrate.[4] Despite various attempts the polyiodide-starch complex has not been unambiguously structurally characterized. This is mainly due to its amorphous nature, which renders structural characterization at atomic resolution impossible. However there exists some solid-state (mainly single crystal X-ray crystallographic) studies on iodine or polyiodide species trapped (clathrated) inside confined spaces offering at least some level of analogy with the elusive starch-iodine complex structure. Organic cations[39] as counter ions for polyiodide complexes have been published in macrocyclic thioureas,[40] metal complexes[41] and metal-organic frameworks.[42] Very recently a single crystalline pyrrolopolyene-iodine complex where the crystal structure contains infinite polyiodide I$_5$ chains trapped in between the pyrrolopolyene stacks has been reported.[43]

The role of halogen bonding (XB) has mostly been neglected when designing the analogues of the iodine-starch complex. This is somewhat surprising since iodine (I$_2$) is an excellent halogen bonds donor, and thus XB could play a role in the formation of the I$_2$-starch complex. Halogen bonding is the ‘long-lost brother’ of hydrogen bonding (HB) and has been found to playing a major role especially in material science and crystal engineering[44], and has recently been defined by IUCr.[11] The XB and HB have many similarities, particularly in terms of the bond strength and directionality.[12] Due to its strong XB donor ability I$_2$ has a tendency to form strong halogen bonds. A strong charge-transfer (CT) complex is formed when equimolar amounts of molecular I$_2$ and triphenylphosphine are mixed together, where P-I halogen bond was the force featuring CT interaction.[13] Triodide, being a product of between I$_2$ and I$, is generally regarded to contain the strongest halogen bond known with bonding energy about 150 kJ/mol, as high as weak covalent bonds.[14] Polyhalides, in particular polyiodides, of different lengths were constructed, where halogen bonds occur between iodide anion and the neutral iodine molecules.[15] Heteropolyhalide dianion Cl$^-$•••I$^-$•••Cl$^-$ has been used to construct the solely halogen bonded dimeric capsule.[16] Not only with anionic species or other elements as electron donors, I$_2$ can interact with itself via I-•••I-I halogen bonds, which are the main interaction between the I$_2$ molecules in iodine single crystals.[17] Such intermolecular halogen bonds assemble the iodine molecules into layers, which makes it as a 2D semiconductor.[18] Some structures containing extended halogen-bonded iodine networks were also reported. In most of the cases, the extended I$_2$ chains were just entrapped in the lattice as co-crystalizer. While, a zig-zag I$_2$ chain captured by a tubular MOF via solid-vapor reaction was reported in 2008 by Gao’s group, although they didn’t specifically mention the halogen bonding as a notable interaction.[19] Actually, in the Gao work, each I$_2$ molecule serves both as a halogen bond donor at one end and as a halogen bond acceptor at the another. Among the reported iodine chain structures, no helical halogen-bonded I$_2$ chain structure has been known so far.

For this study, we postulated that a simple diammonium salt, here 1,8-diammoniumoctane hydrochloride (DAO-HCl), with enough conformational flexibility would be able to act as a clathrand for iodine I$_2$ (clathrate forming substance) forming a helical channel through charge-assisted H$_2$N$^+$-H$^+$-Cl$^-$ hydrogen bonds, similarly as urea is doing through the HN-H$^+$-O=C hydrogen bonds in urea inclusion compounds.[20] To our surprise the I$_2$ molecules interact with each other via weak •••I-•••I-I-•••I-I halogen bonds forming a one-dimensional helical chain of iodine molecules inside the trigonal helical channels (Scheme 1) formed by the DAO-HCl salt. In addition to the charge-assisted H$_2$N$^+$-H$^+$-Cl$^-$ hydrogen bonds and weak I-•••I halogen bonds, strong I-I•••Cl halogen bonds were observed between the chloride anions in the channel wall and the channel residing iodine molecules. The trigonal channels share walls with the neighbors and form additional smaller hexagonal channels which also
entraps iodine molecules (Scheme 1). The trigonal helical hydrogen bonded DAO-HCl channel is very similar with the helical channel of starch. The arrangement of molecular iodine inside DAO-HCl is thus reminiscent to the polyiodide-starch complex and offers an alternate structural model for the single crystalline pyrroloperylene–iodine complex of the iodine structure in the well-known yet structurally uncharacterized starch-iodine system.

Methanol solution containing two equivalent molecular iodine was mixed with the methanol solution of 1,8-diammoniooctane with excess of hydrochloric acid (0.2 M). Evaporation of the solvent produced brown needle-like crystals suitable for single-crystal X-ray diffraction. The system crystallizes in the trigonal space group R-3 so that one DAO-HCl interacts with 2.2 I₂ molecules trapped inside two structurally different channels, so that the contents of iodine is 72% in the structure. In the trigonal channels (Figure 1A) each iodine molecule interacts with the chloride anion at the wall of the channel molecule via strong I-...I=Cl- halogen bond (R₂= 0.82)²¹ while the remaining iodine forms a weaker I=I-...I=I- halogen bonds to the adjacent I₂ molecule with R₂= 0.90. The ••I-••I-••I- halogen bonds link the I₂ molecules in a helical manner, thus forming a halogen-bonded I₂ helix (Figure 1A, 2B and S1). The XB angles, I=Cl...I=Cl (174.18(5)°) and I-...I=Cl (174.24(3)°) reflect the true nature of the halogen bonds (Figure 3). Every three iodine molecules consist of a turn in the helices with the pitch of 4.6069(5) Å equal to the crystallographic c axis. The triangular prism shape of the channel has the diameters of the inscribed and circumscribed circle of ca. 5.8 and 11.6 Å, respectively. The centrosymmetric space group in the current structure reflects the mixture of the right handed and left handed chains.

In the structure the DAO moiety adapts the gauche conformation instead of the more common anti and results in both the geometry and size match between the trigonal DAO-HCl channel and the iodine guests. The hexagonal channel is too small to comfortable accommodate full I₂ molecule, thus this channel shows partial (0.2) occupancy of I₂ (Figure 1B).

Due to the strong intermolecular halogen bonds the packing coefficient for the iodine molecules inside the trigonal channel is 61%,²²,²³ considerably higher than the Rebek’s 55% rule (Figure 1A).²⁴ The strong XB interactions are also evident from the visual puncture of the trigonal channel cavity surface²⁵ (Fig. 1A) and electrostatic potential picture (Figure 3B).²²

![Figure 1. The channel space (grey) with entrapped I₂ in CPK style in the trigonal channel (A) and hexagonal channel (B).](image1)

![Figure 2. The hydrogen bonding helical channel (A) and halogen bonding with helical arrangement of the I₂ molecules inside the trigonal channel (B). Each color represents one turn of the helix.](image2)

![Figure 3. The geometric parameters of the halogen bonded molecular iodine inside the trigonal channel (A) and the ESP picture mapped onto the electron density isosurface of 0.005 e(au)³ to show the interaction contact and the clear σ-hole (B).](image3)
A more detailed inspection reveals that the interactions between the I₂ molecules inside the trigonal channels are the same as found in the solid iodine. The 110 K X-ray diffraction data for solid iodine\(^{[17]}\) indicated the layer arrangement of the iodine molecules. The closest iodine molecules from different layers have the shortest I—I distance of ca. 4.28 Å, much larger than the sum of van der Waals radius of 3.96 Å. In the layer, each iodine atom interacts with two neighbours. Both the I—I distance (3.5010 Å) and the I—I angles (170.05 and 105.81 °, respectively) imply the XB interactions (Fig. S2). Such XBs significantly elongate the I—I bond length to 2.715 Å, compared with that of 2.662 Å in gas phase. All these geometric parameters are highly consistent with the current case. The only slight difference is the relative orientation of the three iodine molecules (Fig. S2). Accordingly, the organization of the I₂ molecules inside the trigonal channel is like an isolated chiral 1-D chain of iodine molecule of the solid iodine structure.

The formation of the I₂ XB helix is unprecedented as it results from spontaneous assembly of the components, DAO-HCl and I₂. The gauge conformation of the DAO enables us to reason the origin of the channelled structure. A simple force field calculation\(^{[25]}\) was performed to optimize the geometry of the helical arrangement of the components taken from the X-ray structure. The resulted energy-minimum geometry slightly changed the conformation of the DAO where the C-N bonds have to rotate for the formation of the H₂N—H—I•••Cl bridge as demonstrated in Figure S5. Due to this the modelled structure shows a 3-fold axis instead of the 3; screw axis observed in the DAO•HCl-I₂ crystal structure. Although the modelled circular structure gave the energy minima comparable to the circularly helical DAO•HCl-I₂ structure, it doesn’t favour the structural extension to 3-D.\(^{[26]}\) For comparison, we also conducted the geometry optimization for the cis-conformation of the DAO-HCl. In the regular cis-form chain of a \(\alpha\omega\)-diammoniumalkane (\(\alpha\omega\)-DAA) with even number of carbon atom, the two -NH₂ groups at both ends are staggered. Accordingly, the H₂N—H—I•••Cl bridges at the joint were built at the expense of twisting the DAO chain, resulting in helical arrangement. The helicity is more obvious in the shorter \(\alpha\omega\)-DAA with even carbon number (Figure S6). The idea was further supported by the similar simulation for (\(\alpha\omega\)-DAA-HCl)\(_2\), where the chain bears odd number carbon atoms, and the two -NH₂ group at both ends are in eclipsed mode (Figure S7). Then the H₂N—H—I•••Cl bridges were constructed directly, and the \(\alpha\omega\)-DAA-HCl) structure show \(\bar{D}\) point group.

The hydrogen bonded helical trigonal channels share a wall with all the neighbours, then six such channels create an additional hexagonal channel (Scheme 1). The difference Fourier map show electron density peaks, which are modelled as highly disordered iodine molecules. The geometry of these electron density peaks shows an average distance of 2.75 Å, which is the I—I bond distance of I₂ molecule. In addition there are also weak I—I•••Cl contacts to the wall of the hexagonal channel with average I•••Cl distance of 3.52 Å (Figure S3). Each iodine molecule in the hexagonal channels contacts with one Cl⁻ anion at each end, formally becoming a \([\text{Cl}\text{I—I•••Cl}^{-}]\) species (Figure 1B, S4). The structurally unstable \([\text{Cl}\text{I—I•••Cl}^{-}]\) dianions have previously found to be stabilized by the hydrogen bonded framework in a sulfadiazine hydrochloride salt.\(^{[27]}\) The \([\text{Cl}\text{I—I•••Cl}^{-}]\) dianions have also been successfully used to construct the first purely halogen bonded dimeric capsule structure.\(^{[16]}\) The average C—I•••Cl distance in this case was about 9.8 Å, very similar with that of the reported ones.\(^{[16, 27]}\)

The phenomenon in the DAO-HCl-I₂ of iodine molecules entrapped in the helical organic channel evokes the comparison the iconic starch-iodine system. The similar size of the helical channels\(^{[28]}\) might guide the similar arrangement of the inclusion iodine. In the starch-iodine system, the sugar amylose was proposed to form a helical tunnel embracing the iodine, as I₁, presenting a characteristic blue colour. In 2016, Wudl \textit{et al.} reported an almost linear infinite iodine chain complex where the interatomic I—I distances vary from 3.054 to 3.174 Å.\(^{[26]}\) The Raman spectroscopy of the Wudl complex compared with the reported values of starch-iodine suggested the infinite iodine chains also exists in starch-iodine structure. Linear polyiodides have been occasionally reported,\(^{[29]}\) nevertheless, the interactions between the iodine molecules remain elusive. With this in view the current DAO-HCl-I₂ structure with infinite halogen bonded chain of iodine molecules could provide more understanding on the structural features of iodine in starch. Raman spectra was recorded to investigate the state of iodine molecules in DAO-HCl-I₂. Two strong peaks at 119.9 cm⁻¹ and 155.6 cm⁻¹ were shown (Figure 4). The low-frequency signals indicate the single bond in iodine was significantly weakened, although the geometry of both the intra-I-I and inter I-I in the halogen bonded chain are very similar with that in solid iodine. Such low-frequency signals are also very similar with those found in starch-iodine system (109 cm⁻¹ and 163 cm⁻¹, respectively).\(^{[30]}\)

In conclusion, the halogen bonded I₂ helical chain forms through entrapment in a hydrogen bonded helical channel. The \(-\text{I—I•••I—I•••Cl—}\) halogen bonds play an important role in the construction of the helical 1-D iodine chain. The strong H₂N—H—I•••Cl hydrochloride in \textit{gauche} conformation allow the helical channel formation. The structure of the DAO-HCl-I₂ complex determined through single crystal X-ray diffraction experiment and the
Experimental Section

All the chemicals in this work were commercially available and used without additional treatment. Single crystals of the helix were obtained by evaporation of 4 ml methanolic solution containing 0.1 mmol 1,8-dianionniummontane (14.4 mg) and two drops of concentrated hydrochloric acid (around 1 mmol), to which 4 ml methanol solution of 0.2 mmol iodine (50.8 mg) was added. The crystal was measured using an Agilent SuperNova dual wavelength diffractometer with multilayer optics monochromatized Mo-Kα (λ = 0.71073 Å) radiation from a micro-focus X-ray source at 100 K. CCDC-1895019 contains the supplementary crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Raman spectroscopy was performed using a Thermo Scientific DXR instrument equipped with a 532 nm laser. The electrostatic potential was derived from the single point energy calculation with DFT/B3LYP method and 6-311+G** basis set. The geometry was from the single crystal X-ray structure. MMFF method was used for the force field calculations. The packing coefficient of 61% for the trigonal channel was achieved from the theoretical volume of the molecular iodine (64 Å³, taken from Spartan' 16) divided by the corresponding space volume (104 Å³, calculated with Olex2 by omitting the inside I₂ molecule with probe radius of 1.2 Å and grid size of 0.2 Å).

Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China (NSFC, FP: grant no. 21602071), the Fundamental Research Funds for the Central Universities (FP: grant no. CCNU17QN006), Central China Normal University, China, and the University of Jyväskylä, Finland. This work was supported by the Program of Introducing Talents of Discipline to Universities of China (111 program, B17019).

Keywords: clathrate • halogen bonding • hydrogen bonding • iodine • supramolecular chemistry


This article is protected by copyright. All rights reserved.
COMMUNICATION

Entry for the Table of Contents
Layout 1:

COMMUNICATION

Text for Table of Contents

Author(s), Corresponding Author(s)*

Page No. – Page No.

Title

Layout 2:

COMMUNICATION

Fangfang Pan,* Yingchun Chen, Siyu Li, Minzhi Jiang, and Kari Rissanen*

Page No. – Page No.

Iodine Clathrated: A Solid-State Analog of the Iodine-Starch Complex

The clathration of the I-•••I-I•••I-I halogen-bonded iodine (I₂) helices inside the helical channels formed by 1,8-diammoniumoctane chloride was reported. The structure shows a marked similarity with the well-known starch-I₂ system, and thus may provide insight for the yet unresolved structure of the I₂ in the helical starch channel.