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Halogen Bonds with Coordinative Nature: Halogen Bonding in a S-I$^+$-S Iodonium Complex

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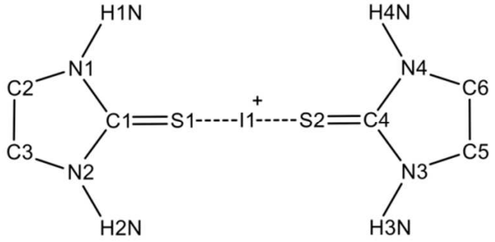
A detailed study of unexpectedly strong iodonium to sulfur halogen bonds in $[I(2\text{-imidazolidinethione})_2]^+$ is presented. The interactions are characterized by single crystal X-ray diffraction, charge density analysis based on QTAIM calculations, mass spectrometry, and NMR spectroscopy. The results, small R_{IS} = 0.7 and high interaction energy of -60 $kJmol^{-1}$, support a coordinative nature of halogen bond between the iodonium ion and sp^2 hybridized sulfur atoms.

Introduction

In the recent years growing attention has been focused on halogen bonding (XB)[1], stimulated by its intriguing properties, such as strong directionality, specificity and strength comparable to hydrogen bonding (HB).[2] Recently, this "long lost brother"[3] of hydrogen bonding has been found to have wide variety of applications.[4] Halogen bonding has, however, stayed relatively unrecognized and unexplored non-covalent interaction, and despite of the increasing amount of both theoretical and experimental studies[3,5], its true nature still lacks comprehensive explanation.

A halogen bond is defined to be an interaction between an electrophilic region of a polarized halogen atom (XB donor) and a nucleophilic region (XB acceptor) in another, or the same, molecular entity.[1] The interaction between the donor and acceptor is considered to be mainly electrostatic, but the definition of halogen bond covers almost any type of non-covalent electron donor – electron acceptor contacts involving halogen atoms.[1] The most commonly used halogen bond acceptors are sp^3- and sp^2-hybridized nitrogen atoms and halide anions.[2] They often give stronger XB interactions than the substantially less investigated oxygen, sulfur, selenium and covalently bound halogen atoms (in metallates), whose capacity to act as halogen bond acceptors often depends on the nature of the XB donor.[6] Because of the electrostatic nature of the halogen bonds,[7] systems where either the XB acceptor or the donor moieties are charged exhibit typically substantially stronger interactions compared to neutral assemblies. Anionic XB acceptors, such as halides[8], polyhalides[9] and metal complexes[10], are commonly used to construct strong halogen bonding interactions, and therefore they are particularly useful building blocks in supramolecular architectures. For example $C_6F_5I\cdots Cl^-$ halogen bonding system exhibits interaction energy ΔE as high as -108 $kJmol^{-1}$.[11] Regardless of their interesting properties, the cationic XB donors are much less studied than anionic XB acceptors. Herein, we describe a synthesis of a iodonium complex $[I(2\text{-imidazolidinethione})_2]^+ \cdot ½I^- \cdot ½[I_3]^-$ (**1**) and a thorough structural and computational analysis of the strong $I^+\cdots S$ halogen bonds between a iodonium cation (XB donor) and the sulfur atom in a thione group (XB acceptor). The formation of I^-, $[I_3]^-$ and I^+ ions in **1** is caused by a heterolytic cleavage of a diiodine through a charge-transfer (CT) complex 2-imidazolidinethione-2(I_2).[12] Thioamides and thiones are known to be powerful electron donors for CT complexes of iodine,[13] capable of effectively delocalizing the partial positive charge over the rest of the molecule. Usually this causes lengthening of the C=S double bond of the thione group (Scheme 1).[14]



Scheme 1. The schematic structure and numbering of complex **1**. The positive charge is distributed over the whole molecule but has been drawn only on iodine for clarity.

Table 1. Crystallographic data for compound **1**.

Empirical formula	$C_6H_{12}IN_4S_2 \cdot 0.5I_3 \cdot 0.5I$
Fw (g/mol)	585.02
Temp (K)	100(2)
λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pccn
a (Å)	14.4457(4)
b (Å)	14.5288(3)
c (Å)	13.7814(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2892.42(12)
Z	8
ρ_{calc} (Mg/m^3)	2.687
μ (Mo Kα) (mm^{-1})	6.751
No. reflns.	47977
No. param.	153
Unique reflns.	7055
GOOF (F^2)	1.157
R_{int}	0.0268
R1^a ($I \geq 2\sigma$)	0.0203
wR2^b ($I \geq 2\sigma$)	0.0394

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Table 2. The selected bond lengths [Å] and angles [°] for **1**.^{a}

S(1)-I(1)	2.6279(5)	I(1)-H(4N)#	2.88(3)
S(2)#-I(1)	2.6297(5)	N(1)-C(1)	1.328(2)
C(1)-S(1)	1.714(2)	N(2)-C(1)	1.326(2)
C(4)#-S(2)#	1.721(2)	N(4)#-C(4)#	1.324(2)
I(1)-H(2N)	2.91(3)	N(3)#-C(4)#	1.326(2)
S(1)-I(1)-S(2)#	178.119(15)	C(1)-S(1)-I(1)	102.28(6)
H(2N)-I(1)-H(4N)#	174.0(8)	C(4)#-S(2)#-I(1)	100.52(6)

^{a}Symmetry transformations used to generate equivalent atoms. # x, y, -1+z.

Results and discussion

In the crystal structure of **1**, a iodonium cation is slightly asymmetrically coordinated by two 2-imidazolidinethione (etu) ligands (S(1)-I(1) 2.6279(5) Å and S(2)-I(1) 2.6297(5) Å) forming an almost linear (178.119(15)°) S···I$^+$···S linkage (Scheme 1, Table 1, Table 2 and Figure S1). The bond lengths and angles are similar with the structural parameters previously reported for S···I$^+$···S compounds, in which the S-I distances vary between 2.6 and 2.7 Å, and the S-I-S angles between 171 and 180°.[13]

The R_{XB} ($R_{XB}=d_{XB}/(X_{vdw}+B_{vdw})$) ratio can be used as a guideline for a search of strong halogen bonds.[15] In the R_{XB} the distance between the donor and acceptor, d_{XB} [Å], is divided by the sum of vdW radii [Å] of the donor (X) and the acceptor (B). However, it should be kept in mind that the distance between the donor and acceptor does not linearly correlate with the interaction strength. For complex **1** the R_{IS} is 0.7 indicating an unusually strong halogen bond between the sulfur and the iodine.

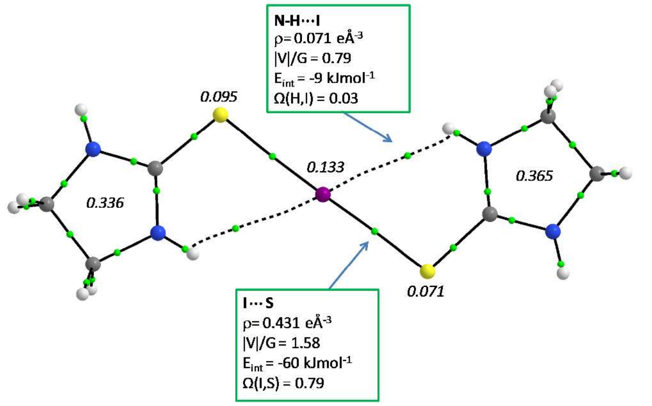
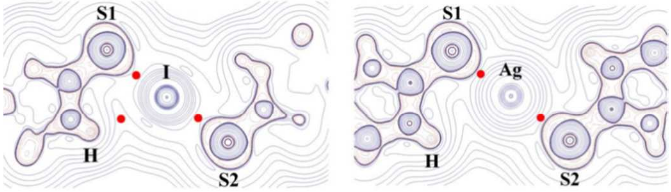


Figure 1. The selected parameters of the electron density for the model of **1** at the bond critical points (BCPs). ρ = electron density; V = potential energy density; G = kinetic energy density; E_{int} = interaction energy; Ω = delocalization index = number of electrons shared between the two (bonding) atoms. AIM atomic charges are shown in italics. (H = white, C = grey, N = blue, S = yellow, I = purple)

The strength and nature of the halogen bonding in solid state of **1** was analyzed in details by the QTAIM (quantum theory of atoms in molecules) method.[16] The non-optimized, experimental structure was used for calculations of electron density distribution on **1** (Figure 1). In literature QTAIM method has been assessed to be one of the most useful methods to quantitatively estimate XB.[17] The QTAIM results show that the I···S interactions in **1** represent an example of a strong bond with interaction energy of -60 kJmol^{-1} at the I···S bond critical point (BCP). Typically, the strength of halogen bonds ranges between -5 and -180 kJmol^{-1} thus being comparable with the strength of hydrogen bonds.[2] Based on the $|V_{BCP}|/G_{BCP}$ ratio of 1.58 (V is the potential energy density and G kinetic energy density) the computational analysis indicates clearly that even if there is considerable electrostatic nature in the I···S contact it is not purely electrostatic. For a typical non-covalent (ionic) interaction the $|V_{BCP}|/G_{BCP}$ ratio should be less than 1 and for a true covalent bond more than 2.[18] Also, the delocalization index Ω(I,S) of 0.79 shows considerable amount of electron sharing between the iodine and two sulfur atoms. The delocalization index describes the average number of shared electrons between (bonding) atoms at BCP.[16,19]

Since the covalent character in the interaction between the iodonium and sulfur atoms proved to be substantial, we compared the results of the charge density analysis to a structurally analogous coordination complex $[Ag(etu)_2]^+$ with a S-Ag$^+$-S moiety.[20] The thione ligands are known to form readily coordination complexes with the d-block metal cations, such as Ag$^+$, Au$^+$, Cu$^+$ and Hg^{2+}.[21] The QTAIM analysis was again carried out by using the non-optimized, experimental geometry. The QTAIM analysis showed that the interaction energy, E_{int}, of the Ag-S bond in $[Ag(etu)_2]^+$ is -105 kJmol^{-1} indicating a strong coordinative metal-ligand bond. The comparison of S···I$^+$···S and S-Ag$^+$-S interactions revealed that the key parameters of the electron density at the bond critical points are very similar for both compounds (Figure 1 and Figure S2). The delocalization index Ω for both complexes indicates similar degree of electron sharing between the interacting atoms (0.79). The I$^+$···S interaction has a somewhat higher $|V_{BCP}|/G_{BCP}$ ratio than the corresponding Ag$^+$-S bond (I$^+$···S: 1.58 and Ag$^+$-S: 1.30) thus being more covalent in nature. The charge distribution in **1** resembles closely the charge distribution found in the silver complex, which further underlines the similarities between these two species. Most of the positive charge in compound **1** is distributed over the etu ligands but the iodine atom still exhibits a distinct positive charge (Figure 1) and can still be seen as I^+ ion halogen bonded to sulfur.

Conventionally, a halogen bond is defined as an electrostatically-driven non-coordinating interaction between an electrophilic region of a halogen atom and a nucleophilic Lewis base.[1] However, in recent years both theoretical[22] and experimental[23] findings indicate that in the case of extremely strong XB donors, *e.g.* halonium ions, the nature of the interaction surpasses the definition of classical halogen bond due to significant covalent contribution. Symmetrical $N\cdots I^+\cdots N$[23-25] and $S\cdots I^+\cdots S$[13] motifs with strong 3-center-4-electron halogen bonds provide good examples of this type of halogen bonding. However, the nature of these interactions has not been rationalized in details. If the interacting motifs form asymmetrical $B\cdots I^+\cdots B$ system (B is the Lewis base) the assembly tends to have one classical covalent and one classical halogen bond.[24,25] In the current study the main properties of the bond critical point between the bonding atoms in the symmetrical $S\cdots I^+\cdots S$ system and its similarities with the true coordinative $S\text{-}Ag^+\text{-}S$ system reveal the dual nature of the $S\cdots I^+$ contacts. In fact, the $S\cdots I^+$ interactions are closer to a classical coordination bond than a pure conventional halogen bond. This type of halogen bonds with strong coordinative nature can be seen as intermediates between classical coordination and classical halogen bonds, and as such offer a limiting case for the description of halogen bonding.



(a) (b)

Figure 2. The Laplacian of the electron density along the S···I···H-N plane of the model $[I(etu)_2]^+$ (a) and along the S···Ag···H-N plane of the model $[Ag(etu)_2]^+$ [20] (b). The red dots represent the I···S, H···I and Ag···S bond critical points (BCPs).

In addition to the halogen bonds with nucleophilic sulfur atoms, the strongly polarized iodine atom I(1) in **1** is further interacting with electrophilic hydrogens H(2N) (I(1)-H(2N) 2.91(3) Å) and H(4N) (I(1)-H(4N) 2.88(3) Å) forming weak $H\cdots I^+$ hydrogen bonds (Figure 2). This is a clear indication of strong polarization of electron density around the I^+ cation. The electron density is accumulated around the $S\cdots I^+\cdots S$ axis making it available for hydrogen bonds. The bond angles of the interactions, H(2N)-I(1)-S(2) 118.9(5)° and H(4N)-I(1)-S(1) 114.1(5)°, are in agreement with the observed directional preferences for the interactions between halogens and electrophiles.[7] The hydrogen bonding interaction was confirmed by AIM analysis (Figures 1 and 2). In the iodonium complex **1**, the polarization is clearly observed in the Laplacian 2-D electron density map (Figure 2), where the electron density lobes point to the direction of the N-H group of the etu ligands. These N-H···I interactions stabilize the almost co-planar arrangement (the I(1)-S(1)-C(1)-N(2) torsion angle is 11.8(2)°) of the iodine atom and the plane of the N-C=S bond. The N-H···I interaction is a typical hydrogen-bonding interaction, with minimal amount of electron sharing and rather weak strength of -9 $kJmol^{-1}$. As expected, the AIM analysis did not show similar intramolecular hydrogen bonding for the $[Ag(etu)_2]^+$ complex, which is an indication of weaker polarization of the Ag^+ compared to I^+. In the case of $[Ag(etu)_2]^+$, there simply is no accessible electron density for additional hydrogen bonding.

Further characterization of **1** by ^1H and ^{13}C NMR spectroscopy indicated the stability of the XB iodonium complex also in the solution. The NMR resonances of **1** shifted downfield relative to the free etu ligand indicating a iodonium to thione sulfur interaction (Figures S3 and S4).[25] The UV-Vis spectrum of **1** exhibited a new absorption band at 359 nm assigned to charge-transfer from the HOMO of the thione to the LUMO of the iodonium ion, indicating the formation of an adduct (Figure S5).[13d-e,26]

The stability of **1** in the gas-phase was analyzed by mass spectrometric measurements. Dissolved crystals of **1** produced a spectrum showing the most abundant peaks corresponding to $[I(etu)_2]^+$ (*m/z* 330.9) and $[I(etu)]^+$ (*m/z* 228.9) ions (Table S1 and Figure S6). The stability of **1** was evident in a collision induced dissociation (CID) experiment, in which the isolated $[I(etu)_2]^+$ tolerated relatively high collision energies, displayed a structure related dissociation pattern and dissociated by subsequent losses of one etu molecule producing fragment ions $[I(etu)]^+$ and a charge-transfer product $[(etu)]^+$ (Figure S7). The XBs are conventionally analyzed in the solid state and in solution, and contrary to other non-covalent interactions only limited amount of gas-phase experimental evidence is published.[27] The current MS study offers invaluable information about the $I^+\cdots S$ halogen bond, indicating the prominent halogen bond donor properties of halonium cations and supporting the results obtained by QTAIM.

Experimental

Materials and methods

2-Imidazolidinethione (etu) (Aldrich, 98%) and iodine (Merck, 99.5%) were commercially available and were used as received. The elemental analysis was determined by VarioMICRO V1.7 instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured with a Bruker Avance 400 MHz spectrometer (Figures S3 and S4). UV-VIS spectrum was measured in CH_3CN with a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer (Figure S5). The mass spectrometric experiments (Table S1, Figures S6 and S7) were performed with a QSTAR Elite ESI-TOF mass spectrometer equipped with an API 200 TurboIonSpray ESI source.

Synthesis and analysis

2-Imidazolidinethione (32.2 mg, 0.315 mmol) and I_2 (80.0 mg, 0.315 mmol) were dissolved in CH_2Cl_2 (15.0 mL). The mixture was stirred at +4°C for 24 h affording a red solution and small amount of brown precipitate. The precipitate was filtered, dissolved to CH_2Cl_2 and combined with the solution. Slow evaporation at room temperature gave dark crystals of $[I(2\text{-}imidazolidinethione)_2]^+\cdot ½I^-\cdot ½[I_3]^-$ (**1**). Yield 90.6 mg, 98.3%. mp 119-120°C. Found: C, 12.14; H, 2.10; N, 9.41; S, 10.54%.

Calc. for $C_6N_4S_2H_{12}I{\cdot}0.5I{\cdot}0.5I_3$: C, 12.32; H, 2.07; N, 9.58; S, 10.96%. λ_{max} (CH_3CN)/nm 245, 294 and 359. δ_H (400 MHz; CD_3CN; Me_4Si): 7.30 (4H, s, NH); 3.79 (8H, s, imidazole) ppm. $\delta_{C\{1H\}}$ (400 MHz; CD_3CN; Me_4Si): δ 175.44 (S=C); 46.46 (imidazole) ppm. The stability of **1** in solution was further confirmed as the downfield-shifted methylene proton resonances in MeOD (etu: 3.65 ppm, **1**: 3.83 ppm) are in line with the iodonium to the thione sulfur interaction. ESI-MS: $[(etu)_2+H]^+$ *m/z* 203, $[I(etu)]^+$ 229 and $[I(etu)_2]^+$ 331.

Crystal structure determination

The crystal of **1** was immersed in perfluoropolyether cryo-oil, mounted in a Nylon loop and measured at a temperature of 100 K. The X-ray diffraction data was collected on a Bruker Kappa Apex II Duo diffractometer using Mo Kα radiation (λ = 0.71073 Å). The Apex2[28] program package was used for the cell refinement and data reduction. The structure was solved by direct methods using the SHELXS-97[29] program. A semi-empirical absorption correction (SADABS)[30] was applied to the data. Structural refinement was carried out using the SHELXL-2014[29] refinement program. Both the iodide anion, I(2), and the I(4) of the I_3^- anion lie on independent twofold axis. The NH hydrogen atoms were located from the difference Fourier map and refined isotropically. Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.99 Å, and U_{iso} = 1.2 U_{eq}(parent atom). The structure of **1** is presented in Figure S1 and the selected bond lengths and angles for **1** are presented in the Table 2.

Computational details

All models were calculated with the Gaussian09 program package[31] at the DFT level of theory with a hybrid density functional PBE0[32]. Similar basis sets were selected as in our previous study for gold N-methylbenzothiazole-2-thione (mbtt) structures, which included the standard all-electron basis sets 6-311+G(d) for S atoms, and 6-31G(d,p) for all other atoms.[33] The central iodine in $[I(etu)_2]^+$ or silver atoms in $[Ag(etu)_2]^+$ [20] (Figure S2) were described with the relativistic def2_TZVPPD ECP basis set.[34] The DFT wavefunction was used in the topological charge density analysis with the QTAIM (Quantum Theory of Atoms in Molecules)[16], which was performed with the AIMALL program[35]. The molecule was not optimized but the experimental X-ray structures were packed and several models of different sizes and symmetries were cut to describe each of the crystal structures in order to investigate the effect of local environment around the interesting bond critical points. The larger models showed effectively the same results, which indicates that the environment has very little effect on the intramolecular interactions in the crystal structure.

Mass spectrometry

The mass spectrometric experiments (See Table S1 and Figures S3-S4) were performed with a QSTAR Elite ESI-TOF mass spectrometer equipped with an API 200 TurboIonSpray ESI source from AB Sciex (former MDS Sciex) in Concord, Ontario (Canada). Two crystals of **1** were first dissolved in CH_3CN to obtain ~9 mM stock solution, which was then diluted in 1:10 $CH_3CN/CHCl_3$ to obtain final 90 μM sample for the experiments. The sample was injected into the ESI source with a flow rate of 5 μL/min. The parameters were optimized to get maximum abundance of the ions under study. Room-temperature nitrogen was used as nebulization (30 psi) and as curtain gas (15 psi). The ion-source voltages of 4.5 kV for capillary, 10V for the oriface plate (declustering potential), 5V as potential difference between skimmer and pre-quadrupole and between 250 V for the potential difference between the focusing ring and pre-quadrupole were used. Accumulation delay of 1s, ion release delay of 6 ms and ion release width of 5ms were used. Nitrogen was used as collision target in CID experiments and collision energies between 5 V and 30 V were used to induce fragmentation. Each spectrum was an average of spectra collected within 2 to 5 min, each of these containing 20 individual scans that were averaged before being sent from the instrument to data system. The measurement and data handling was accomplished with Analyst® QS 2.0 Software. Mass spectra were externally calibrated by using sodium trifluoroacetate. The composition of the ions was verified by comparing experimental and theoretical mass values as well as isotopic distributions.

Conclusions

In summary, unusually strong $I^+{\cdots}S$ halogen bonds with small R_{IS} = 0.7 and high interaction energy of -60 $kJmol^{-1}$ were characterized structurally and computationally. Complementary NMR spectroscopy and mass spectrometry studies demonstrate the unexpected strength and stability of $I^+{\cdots}S$ halogen bonds both in solution and in the gas-phase. Previous theoretical and experimental studies have suggested a partial covalent contribution involved in symmetrical $B{\cdots}X^+{\cdots}B$ halogen bonding interactions. In the present study the computational comparison of $I^+{\cdots}S$ interactions to classical coordination bonds between a thione sulfur and a Ag^+ cation in a $S\text{-}Ag^+\text{-}S$ complex indicates that with very strong halogen bonding donor I^+, the halogen bond is no longer merely an electrostatic contact but have a dual nature with considerable coordinative nature. Therefore, this type of $I^+{\cdots}S$ halogen bonds can be seen as limiting cases between the electrostatic interactions and covalent bonds.

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† CCDC 984540 (**1**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic Supplementary Information (ESI) available: crystal structure of **1**, ^{1}H and ^{13}C NMR spectra of **1**, UV-Vis spectrum of **1**, ESI-MS and CID spectra of **1**, and selected properties of the electron density at the bond critical points for the model [Ag(etu)$_2$]$^+$. See DOI: 10.1039/b000000x/

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Halogen Bonds with Coordinative nature: Halogen Bonding in a S-I^+-S Iodonium Complex

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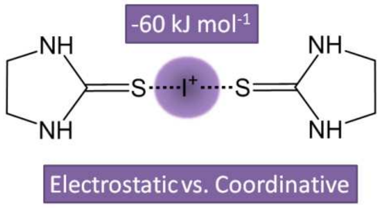
Graphical and textual abstract for the table of contents



A thorough characterization of unusually strong I^+-S halogen bonds indicates that halogen bonding is not merely an electrostatic contact, but has a strong coordinative nature, thus expanding the scope of halogen bonding.