Supporting Information

Halogen Bonds with Coordinative Nature: Halogen Bonding in a S-I⁺-

S Iodonium Complex

Laura Koskinen, Pipsa Hirva^{*}, Elina Kalenius, Sirpa Jääskeläinen, Kari Rissanen^{*} and Matti Haukka^{*}

Table of Contents

Figure S1. Halogen- and hydrogen bonding interactions in 1			
Figure S2. Selected properties of the electron density at the bond critical points for the model $[Ag(etu)_2]^+$	S 1		
Figure S3. ¹ H NMR spectrum of 1	S2		
Figure S4. ¹³ C NMR spectrum of 1	S2		
Figure S5. UV-Vis spectrum of 1	S3		
Table S1. Compositions, theoretical and experimental mass values and mass accuracies of the ions	S3		
Figure S6. ESI-MS spectrum measured from dissolved crystals of 1	S4		
Figure S7. CID spectra measured from isolated $[I(etu)_2]^+$	S4		



Figure S1. Halogen- and hydrogen bonding interactions in **1**. The thermal ellipsoids are drawn at 50% probability.



Figure S2. Selected properties of the electron density at the bond critical points for the model $[Ag(etu)_2]^{+7}$. The properties were calculated according to the Quantum Theory of Atoms in Molecules (QTAIM). 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.



Figure S3. ¹H NMR spectrum of 1 in CD₃CN.



Figure S4. ¹³C NMR spectrum of 1 in CD₃CN.



Figure S5. UV-Vis spectrum of 1 in MeCN.

Table S1. Compositions, theoretical and experimental mass values and mass accuracies of the ions.

Ion	elemental composition	m/z (calc)	m/z (exp)	mass accuracy (<i>m</i> / <i>z</i>)
[(etu) ₂ +H] ⁺	$C_6H_{11}N_4S_2$	203.0420	203.0470	-0.005
[I(etu)] ⁺	$C_3H_6N_2SI$	228.9291	228.9368	-0.008
$[I(etu)_2]^+$	$C_6H_{12}N_4S_2I$	330.9543	330.9629	-0.009



Figure S6. ESI-MS spectrum measured from dissolved crystals of **1** 1:10 CH₃CN/CHCl₃. Insets showing zoomed regions for $[I(etu)_2]^+$ and $[I(etu)]^+$ (calculated isotopic patterns shown with red dotted line).



Figure S7. CID spectra measured from isolated $[I(etu)_2]^+$ at collision energies 5 and 30V.