Supporting Information

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

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Table of Contents

Figure S1. Halogen- and hydrogen bonding interactions in 1 S1
Figure S2. Selected properties of the electron density at the bond critical points for the model [Ag(etu)\(_2\)]\(^+\) S1
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)]\(^+\). The properties were calculated according to the Quantum Theory of Atoms in Molecules (QTAIM). \( \rho \) = electron density; \( V \) = potential energy density; \( G \) = kinetic energy density; \( E_{\text{int}} \) = interaction energy; \( \Omega \) = delocalization index = number of electrons shared between the two (bonding) atoms. AIM atomic charges are shown in italics.
Figure S3. $^1$H NMR spectrum of 1 in CD$_3$CN.

Figure S4. $^{13}$C NMR spectrum of 1 in CD$_3$CN.
**Figure S5.** UV-Vis spectrum of 1 in MeCN.

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

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<th>Ion</th>
<th>elemental composition</th>
<th>m/z (calc)</th>
<th>m/z (exp)</th>
<th>mass accuracy (m/z)</th>
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<td>[(etu)₂+H]⁺</td>
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**Figure S6.** ESI-MS spectrum measured from dissolved crystals of 1 1:10 CH$_3$CN/CHCl$_3$. 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.