1,2-Bis(3-methyl-imidazolin-2-ylium iodobromoselenanide)ethane: Oxidative Addition of IBr at the Se Atom of a >C=Se Group**

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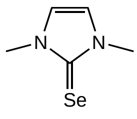
It is well known that chalcogen(II) halides can be stabilized as adducts of Lewis bases.[1] The most common synthetic approach to such adducts is the reduction of chalcogen(IV) halides in the presence of electron pair donors that may also act as reducing agents.[2] An alternative method to such adducts is the oxidative addition of halogens to chalcogen-containing molecules.[3, 4] As an example, addition of Cl_2 to 1,3-dimethylimidazoline-2-thione[5] gives a stable 10-S-3 hypervalent[6–8] "T-shaped" compound featuring a linear Cl-S-Cl group: the product can also be regarded as an adduct between 1,3-dimethylimidazolin-2-ylidene and SCl_2.[7, 9, 10]

No "T-shaped" S adducts with I_2 have so far been reported, whereas two with Br_2 have been structurally characterized only very recently.[11] On the other hand, analogous Se adducts with Br_2 are numerous,[12b–14] and examples with I_2 have recently been reported.[15, 16] However, the reaction of halogens (X_2) with donor molecules containing the $>C{=}E$ (E = S, Se) group do not systematically give 10-E-3 hypervalent "T-shaped" compounds, instead a great variety of products can be isolated depending on the identity of the halogen, the chemical environment around the chalcogen carbonyl group and, in some cases, the nature of the solvent and the reaction conditions.[14] In addition to adducts featuring approximately linear E-X-X groups and X-E-X groups, $[>C{-}E{-}E{-}C<]^{2+}$ dicationic species containing a chalcogen–chalcogen bond, and $[>C{-}E{-}X{-}E{-}C<]^{+}$ cations featuring a central X^{+} ion linearly coordinated by two chalcogenone molecules have also been described.[14] Compounds belonging to the aforementioned structural archetypes can also be isolated from reactions with interhalogens IX (X = Br, Cl), but surprisingly no "T-shaped" adducts featuring I-E-X (E = S, Se) moieties have been reported so far, indicating a very low tendency of interhalogens to undergo oxidative addition to chalcogen donor atoms and in particular to chalcogen carbonyl $>C{=}E$ groups.

Recently, we have studied the reactivity of imidazoline-2-selone derivatives **1**–**3** towards I_2[15a] and Br_2.[13a] Hypervalent "T-shaped" compounds containing Br-Se-Br groups were isolated from the reaction of the three donors with Br_2. Structurally analogous I_2 adducts were isolated only with **1** and **3**, whereas a charge transfer adduct featuring Se-I-I groups was obtained in the case of **2**. We report herein the results of our studies on the reactivity of 1,2-bis(3-methylimidazoline-2-selone)ethane (**3**) with IBr.



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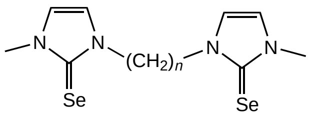

2 (*n* = 1)
3 (*n* = 2)

The reaction of **3** with IBr in MeCN solution in a 1:2 molar ratio gives red-orange crystals of **3**·2IBr after slow evaporation of the solvent. X-ray structure analysis[17] reveals that the compound is the first "T-shaped" selenium adduct featuring I-Se-Br groups (Figure 1). The two I-Se-Br groups are approximately linear; the Se–I bonds are unexpectedly shorter than the Se–Br bonds. Moreover, while the two Se–I bond lengths are similar (2.606(2) in unit A and 2.629(2) Å in unit B, Figure 1), the lengths of the two associated Se–Br bonds differ considerably (2.897(2) in unit A and 2.766(2) Å

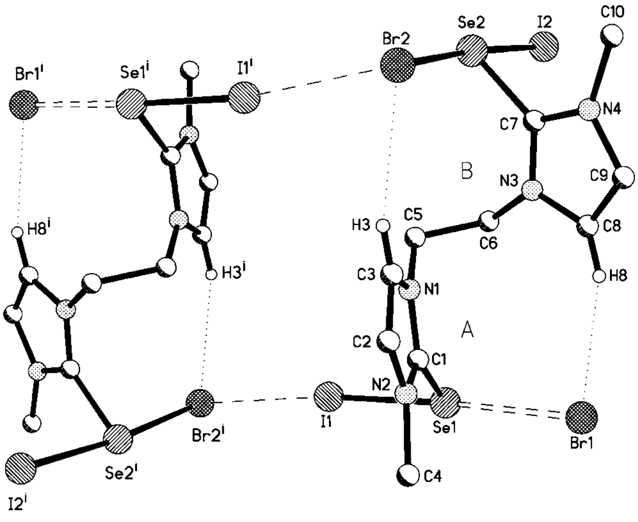

Figure 1. View of a dimeric unit of **3**·2IBr with the numbering scheme adopted. For clarity only those atoms involved in intramolecular hydrogen bonds are shown. A refers to the I-Se-Br system having the longer Se–Br bond (double dashed lines), B to the one with the shorter Se–Br distance. Single dashed and dotted lines denote intermolecular I···Br contacts and intramolecular hydrogen bonds, respectively. Selected bond lengths [Å] and angles [°]: C1-Se1 1.894(9), C7-Se2 1.890(9), Se1-Br1 2.897(2), Se2-Br2 2.766(2), Se1-I1 2.606(2), Se2-I2 2.629(2); C7-Se2-Br2 83.2(3), C1-Se1-I1 95.6(3), C7-Se2-I2 90.6(3), I1-Se1-Br1 175.52(5), I2-Se2-Br2 173.80(5); symmetry code *i*: 2 − *x*, 1 − *y*, 1 − *z*.

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in unit B (shown as double dashed lines in Figure 1)). The conformation of the molecule is determined by two intramolecular hydrogen bonding interactions (shown as dotted lines in Figure 1) that involve the two bromine atoms (Br1 ··· H8 2.743 Å, Br1 ··· H8-C8 160°; Br2 ··· H3 2.855 Å, Br2 ··· H3-C3 155.1°). Furthermore, two symmetry-related $\mathbf{3}\cdot 2\,\mathrm{IBr}$ adduct units interact through I ··· Br contacts (I1 ··· Br2^{i}, 3.601(2) Å shown as single dashed lines in Figure 1) to form dimeric assemblies. The packing of these dimers is determined by long I ··· I and I ··· Se contacts that range from 3.992(2) to 4.115(3) Å.

Since in $\mathbf{3}\cdot 2\,\mathrm{IBr}$ the order of Se–Br and Se–I bond lengths is reversed with respect to that expected on the basis of the atomic radii, density functional theory (DFT) calculations[20] were carried out on the I_2, Br_2, and IBr, Se-hypervalent adducts of **1** as model compounds and on the cations $[\mathbf{1}\cdot X]^+$ (X = I, Br) to understand the nature of the chemical bond in X-Se-Y systems (X, Y = I, Br) and their donor–acceptor and vibrational properties. On the whole, a very good agreement is found between the optimized geometries of the organic frameworks and the corresponding experimental structural data for $\mathbf{1}\cdot \mathrm{Br}_2$,[13b] $\mathbf{1}\cdot \mathrm{I}_2$,[15a] $\mathbf{3}\cdot 2\,\mathrm{Br}_2$,[13a] and $\mathbf{3}\cdot 2\,\mathrm{IBr}$ (see Supporting Information for calculated data). The Se–Br bond length calculated for $\mathbf{1}\cdot \mathrm{Br}_2$ (2.602 Å) is quite close to the mean value observed in the structure of $\mathbf{1}\cdot \mathrm{Br}_2$ (2.575 Å)[13b] and $\mathbf{3}\cdot 2\,\mathrm{Br}_2$ (2.591 Å),[13a] whereas the Se–I bond length calculated for $\mathbf{1}\cdot \mathrm{I}_2$ (2.983 Å) is longer than those found in the structures of $\mathbf{1}\cdot \mathrm{I}_2$ and $\mathbf{3}\cdot 2\,\mathrm{I}_2$ (mean values 2.812 and 2.821 Å, respectively).[15a] As expected the Se–I distance (2.964 Å) is calculated to be longer than the Se–Br distance (2.794 Å) in $\mathbf{1}\cdot \mathrm{IBr}$. The Se–X bond lengths calculated for the $[\mathbf{1}\cdot X]^+$ ions (2.539 (X = Br), 2.722 Å (X = I)) are shorter than those calculated for the hypervalent systems, and this shortening is accompanied by an opening of the C-Se-X angle, which increases from 84.3° in $\mathbf{1}\cdot \mathrm{Br}_2$ to 97.2° in $[\mathbf{1}\cdot \mathrm{Br}]^+$ and from 85.4° in $\mathbf{1}\cdot \mathrm{I}_2$ to 98.3° in $[\mathbf{1}\cdot \mathrm{I}]^+$. The widening of this angle seems to represent the most sensitive structural variation induced in the Se-hypervalent system upon lengthening of one Se–X bond towards the formation of the $[>\mathrm{C{-}Se{-}X}]^+$ ion. In this respect unit A in $\mathbf{3}\cdot 2\,\mathrm{IBr}$ (Figure 1), which has a C-Se-I angle of 95.6(3)°, very close to the value of 98.3° calculated for the cation $[\mathbf{1}\cdot \mathrm{I}]^+$, can be considered as a $[>\mathrm{C{-}Se{-}I}]^+$ ion interacting with a Br^- ion through the chalcogen (Se ··· Br 2.897(2) Å). Unit B, which features a shorter Se–Br bond length (2.766(2) Å) and a C-Se-I angle of only 90.6(3)°, can be regarded as being closer to a purely covalent "T-shaped" system.

Table 1. Calculated NBO charges (e) on the N, C, Se, and halogen atoms in **1**, $\mathbf{1}\cdot \mathrm{I}_2$, $\mathbf{1}\cdot \mathrm{Br}_2$, $\mathbf{1}\cdot \mathrm{IBr}$, and $[\mathbf{1}\cdot X]^+$ (X = I and/or Br).[a]

	1	$[\mathbf{1}\cdot \mathrm{Br}]^+$	$\mathbf{1}\cdot \mathrm{Br}_2$	$[\mathbf{1}\cdot \mathrm{I}]^+$	$\mathbf{1}\cdot \mathrm{I}_2$	$\mathbf{1}\cdot \mathrm{IBr}$
N	– 0.438	– 0.376	– 0.340	– 0.379	– 0.392	– 0.392/ – 0.391[b]
C	0.225	0.216	0.224	0.226	0.271	0.275
Se	– 0.268	0.355	0.354	0.244	0.212	0.259
I				0.051	– 0.393	– 0.387
Br		– 0.074	– 0.449			– 0.447

[a] Although the trend in the calculated NBO charges accounts fairly well for the different polar nature of the Se–I and Se–Br bonds, the natural bond orbitals are not well-suited for getting reliable information on Se–X bond orders, since this localized-bond model tends to give limiting ionic forms according to a Lewis formalism. [b] The I-Se-Br moiety is not exactly perpendicular to the ring plane (Br-Se-C-N dihedral angles 97.27 and – 81.40°). Therefore a slight difference in the charge on the two nitrogen atoms is observed.

On passing from the $[\mathbf{1}\cdot X]^+$ ions to the corresponding "T-shaped" adducts the calculated natural bond orbital (NBO) charges (Table 1) on the organic frameworks remain almost unaltered; the selenium atom is partially positively charged in all cases, while the charges on the halogens become considerably negative. In $\mathbf{1}\cdot \mathrm{I}_2$ and $\mathbf{1}\cdot \mathrm{Br}_2$ the terminal halogen atoms carry a negative charge (– 0.393 for $\mathbf{1}\cdot \mathrm{I}_2$ and – 0.449 e for $\mathbf{1}\cdot \mathrm{Br}_2$; see Table 1) equally distributed over the two halogen atoms. In the case of $\mathbf{1}\cdot \mathrm{IBr}$ a negative charge of – 0.834 e is unevenly distributed over two halogens with – 0.447 e on the more electronegative Br (Table 1). Therefore, the charge distribution calculated on the I-Se-Br moiety in $\mathbf{1}\cdot \mathrm{IBr}$ indicates a more ionic character for the Se–Br bond compared to the Se–I bond.

In $\mathbf{3}\cdot 2\,\mathrm{IBr}$, the intramolecular Br ··· H hydrogen bonding interactions (Figure 1) contribute to a further polarization of the Se–Br bond by stabilizing an increased electronic charge on the Br atom, which leads to the formation of the $[>\mathrm{C{-}Se{-}I}]^+ \cdots \mathrm{Br}^-$ ionic pair. In particular, the two different intramolecular hydrogen bonds stabilize the Br atom at different distances from the selenium atom in units A and B (see Figure 1). In agreement with the calculations, the more ionic the Se–Br bond the shorter the Se–I bond length; in $\mathbf{3}\cdot 2\,\mathrm{IBr}$ the two Br-Se-I groups adopt different intermediate situations between the two limiting cases: purely ionic $[\mathrm{I{-}Se}]^+ \cdots \mathrm{Br}^-$ and purely covalent I-Se-Br. In both systems the polarization of the Se–Br bond is such as to reverse the order of the Se–Br and Se–I bond lengths predicted for a purely covalent model.

The intermolecular I ··· Br contacts responsible for the formation of the dimeric units in the crystal structure of $\mathbf{3}\cdot 2\,\mathrm{IBr}$ are consistent either with the calculated charge distribution on the model adducts $\mathbf{1}\cdot \mathrm{IBr}$ (Table 1) or the more ionic character for the Se-hypervalent system in unit A (Figure 1). Indeed, these contacts involve I1, an atom which should carry a small positive charge (see $[\mathbf{1}\cdot \mathrm{I}]^+$ ion in Table 1), and Br2^{i}, which belongs to the less ionic Se-hypervalent system of the symmetry-related adduct molecule, an atom which should carry a partial negative charge (see $\mathbf{1}\cdot \mathrm{Br}_2$ and $\mathbf{1}\cdot \mathrm{IBr}$ in Table 1). The directionality of these intermolecular I ··· Br contacts (Se2-Br2 · ·· I1^{i} 86.84(4)°) can be explained by the nature of the calculated Khon–Sham HOMO and LUMO (Figure 2) on the basis of a donor/acceptor interaction between the π*-HOMO centered on the Se-hypervalent system in unit A of one adduct molecule and the σ*-LUMO centered on the more ionic I-Se-Br system in unit B of the symmetry-related adduct molecule.

Confirmation of the different bonding situations in the two I-Se-Br systems in $\mathbf{3}\cdot 2\,\mathrm{IBr}$ is provided by FT-Raman and FT-IR spectra (300–100 cm^{-1}) of powdered crystals (Figure 3). Owing to the complexity of both spectra, we have calculated the normal vibrational modes for $[\mathbf{1}\cdot \mathrm{I}]^+$ and $\mathbf{1}\cdot \mathrm{IBr}$ and simulated the sum of their IR (Figure 4) and Raman spectra to make assignments. In the IR spectrum three main groups of bands, centered at 270, 185, and 130 cm^{-1}, can be identified for

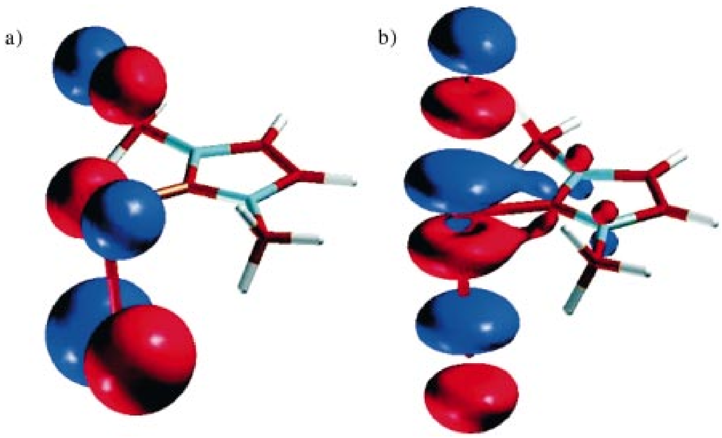

Figure 2. The Kohn–Sham HOMO (a) and LUMO (b) calculated for $\mathbf{1}\cdot$IBr. Neither of them contain any contribution from d orbitals of the Se atom. Therefore, from a Lewis point of view, there is no formal octect expansion and both chalcogen–halogen bond orders have to be considered less than one. The same orbital composition is calculated for $\mathbf{1}\cdot\mathrm{Br}_2$ and $\mathbf{1}\cdot\mathrm{I}_2$.

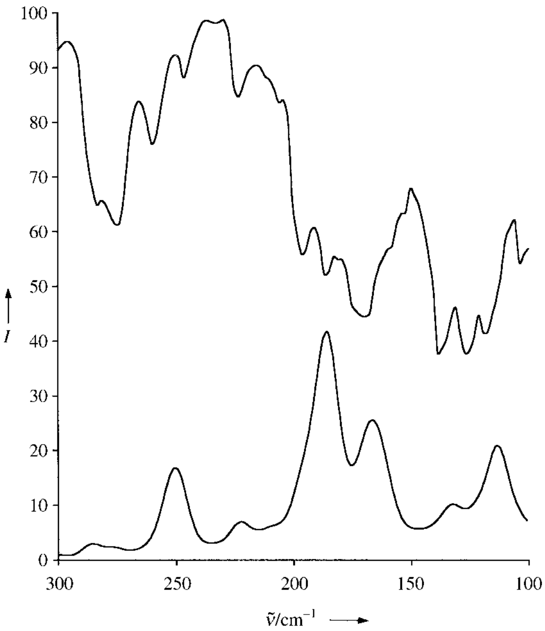

Figure 3. Experimental FT-IR (top) and FT-Raman spectra (bottom) for $\mathbf{3}\cdot$IBr in the low frequency region (100–300 cm^{-1}).

both $[\mathbf{1}\cdot\mathrm{I}]^+$ and $\mathbf{1}\cdot$IBr. The group with the highest frequency can be attributed mainly to a C-Se-I bending mode (279 for $[\mathbf{1}\cdot\mathrm{I}]^+$ and 268 cm^{-1} for $\mathbf{1}\cdot$IBr). The envelope of very strong bands at about 185 cm^{-1} in the simulated spectrum is due to an N-C-Se bending mode in the imidazoline ring plane (196 cm^{-1}) and to the same vibration coupled to the Se–Br stretch (185 cm^{-1}) for $\mathbf{1}\cdot$IBr. The contribution of the N-C-Se bending mode of the cation to this envelope is very small. The two weak bands calculated at 140 and 120 cm^{-1} for $[\mathbf{1}\cdot\mathrm{I}]^+$ and $\mathbf{1}\cdot$IBr, respectively, are mainly due to rotation of the methyl groups coupled with a stretching vibration of the I-Se-Br moiety for $\mathbf{1}\cdot$IBr. Examination of the recorded vibrational spectra for $\mathbf{3}\cdot2$IBr (Figure 3) indicates a good correspondence between the IR and Raman bands, with interesting similarities with the simulated spectrum of Figure 4 (red line), thereby confirming the different nature of the bonds in the two I-Se-Br groups. Evidently, an exact match between the calculated and experimental spectra would be unrealistic because the organic frameworks of $\mathbf{1}$ and $\mathbf{3}$ are different, and

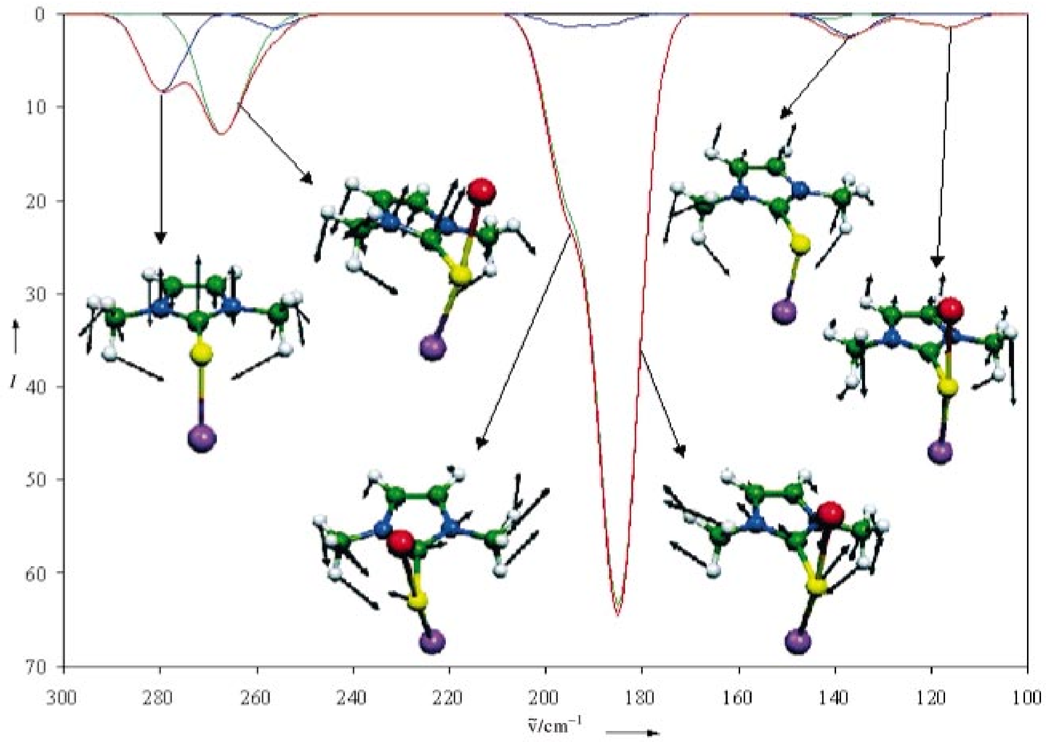

Figure 4. Simulated IR spectrum (100–300 cm^{-1}) based on normal mode DFT calculations for $\mathbf{1}\cdot$IBr (green line), $[\mathbf{1}\cdot\mathrm{I}]^+$ (blue line), and sum of the two (red line), together with representations of the calculated normal modes.

[**1**$\cdot$I]$^+$ and **1**$\cdot$IBr represent the two extremes in the bond nature of these new "T-shaped" adducts: ionic [> C-Se-I]$^+\cdots$ Br$^-$ and covalent I-Se-Br.[29]

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[17] Crystals of **3**$\cdot$2IBr were grown by slow evaporation of a MeCN solution of **3** and IBr in 1:2 molar ratio. Elemental analysis: calcd. for $C_{10}H_{14}Br_2I_2N_4Se_2$: C 15.77, H 1.84, N 7.35; found: C 15.55, H 1.80, N 7.25. Crystal structure analyses: Stoë Stadi-4 four-circle diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, $T = 150(2)$ K, $\theta_{max} = 26°$. The structure was solved by using direct methods[18] and all non-hydrogen atoms were located in subsequent difference Fourier syntheses.[19] Hydrogen atoms were placed in calculated positions and were allowed to ride on their parent atoms during refinement. **3**$\cdot$2IBr: $C_{10}H_{14}Br_2I_2N_4Se_2$, $M_r = 761.79$, triclinic, $P\bar{1}$ (no. 2), $a = 7.767(4)$, $b = 9.940(3)$, $c = 13.524(5)$ Å, $\alpha = 96.41(3)$, $\beta = 106.23(3)$, $\gamma = 106.49(4)°$, $V = 940.4(7)$ Å^3, $Z = 2$, $F(000) = 692$, $\rho_{calcd} = 2.690\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 11.460\ mm^{-1}$, dark red trigonal prism ($0.27 \times 0.27 \times 0.16\ mm^3$). Numerical absorption corrections ($T_{max} = 0.200$, $T_{min} = 0.0807$), 3693 unique reflections, of which 3124 had $I \geq 2\sigma(I)$. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.070P)^2 + 15.93P]$, $P = 1/3[MAX(F_o^2,0) + 2F_c^2]$, was applied. At final convergence $R_1 = (I \geq 2\sigma(I)) = 0.0515$, wR_2 (all data) = 0.1322 for 183 refined parameters, $S = 1.045$, $(\Delta/\sigma)_{max} = 0.347$, $\Delta\rho_{max} = 1.95\ e\,Å^{-3}$ (near heavy atoms). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163716. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[20] Quantum-chemical calculations on isolated molecules of **1**$\cdot I_2$, **1**$\cdot Br_2$, **1**$\cdot$IBr, and [**1**$\cdot$X]$^+$(X = I, Br) were carried out according to DFT[21] using Gaussian 94,[22a] with the hybrid Becke3LYP functional.[23] The basis sets for the calculations on [**1**$\cdot$X]$^+$, **1**$\cdot I_2$, and **1**$\cdot$IBr were the Schafer, Horn, and Ahlrichs pVDZ basis[24] for C, H, N, and Se, while for I and Br we used the Hay–Wadt LANL2DZ basis sets together with effective core potentials.[25] The all-electron former basis set is available for Se and Br but not for the heavier iodine atom. Therefore, in order to be able to compare Se–halogen bonds, the same Hay–Wadt LANL2DZ ECP basis was used for the halogen atoms. In the case of **1**$\cdot Br_2$, SCF convergence problems were found, and although several alternative convergence methods were tried, we were able to achieve convergence only with the 6-31G** basis set. Harmonic IR and Raman frequencies were obtained for **1**$\cdot I_2$ and [**1**$\cdot$X]$^+$ by using the second derivatives of the DFT energy, computed by numerical differentiation of the DFT energy gradients.[22] Finally, NBO calculations[26] were performed for each molecule using the converged density matrix corresponding to the equilibrium geometries. Molden 3.6[27] was used to investigate the shape of the calculated Kohn–Sham orbitals. Calculated unscaled harmonic frequencies were extracted from the output file and converted into a simulated spectrum with the TABFREQ program, using DFT-calculated intensities and a half bandwidth of 10 cm^{-1}. Analysis and drawings of molecular vibrations were performed with the program Molekel.[28]

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