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Charge-Transfer Complexes of *N*-Methylthiazolidine-2(3*H*)-selone (1) and *N*-Methylbenzothiazole-2(3*H*)-selone (2) with I_2 and IBr: Crystal Structures of $1{\cdot}I_2$, $1{\cdot}I_{1.25}Br_{0.75}$, $2{\cdot}2I_2$, and $2{\cdot}2IBr$

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In CH_2Cl_2 solution, *N*-methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) and *N*-methylbenzothiazole-2(3*H*)-selone (**2**) react with molecular diiodine to form 1:1 adducts. From solutions having **1** and diiodine in a 1:1 molar ratio, a neutral charge-transfer compound of formula $\mathbf{1}{\cdot}I_2$ ($C_4H_7I_2NSSe$; **I**) has been obtained, whereas, in the same conditions, **2** yields the previously described ionic compound $[(\mathbf{2})_2I]^+I_3^-$, having the $\mathbf{2}{\cdot}I_2$ stoichiometry. The crystals of **I** are monoclinic [space group *Cc* with $a = 16.400(7)$ Å, $b = 5.976(3)$ Å, $c = 12.942(4)$ Å, $\beta = 127.66(2)°$, $Z = 4$, and $R = 0.024$] and contain units formed by one diiodine molecule bonded almost linearly [177.49(3)°] to the selenium atom. From solutions having a 1:2 molar ratio between the selonic compounds and diiodine, *N*-methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) affords again the same **I** adduct, whereas **2** yields a crystalline compound with formula $\mathbf{2}{\cdot}2I_2$ ($C_8H_7I_4NSSe$; **III**). The crystals of **III** are triclinic [space group $P\bar{1}$, with $a = 11.439(4)$ Å, $b = 14.337(4)$ Å, $c = 16.479(6)$ Å, $\alpha = 115.47(2)°$, $\beta = 97.02(3)°$, $\gamma = 97.85(3)°$, $Z = 6$, and $R = 0.028$]. Unexpectedly, this compound is not ionic as $[(\mathbf{2})_2I]^+I_3^-$, and contains three independent $\mathbf{2}{\cdot}2I_2$ molecular adducts per asymmetric unit. In each molecular adduct, one diiodine molecule is almost linearly bonded to the selenium atom and lies essentially in the plane of the organic molecule. These units are packed in the crystal on parallel stacked planes separated by "graphite-like" interactions, between the organic molecules. The other weakly interacting diiodine molecules fall out of the planes and fit into the cavities left in the packing. In the same solvent and for a 1:1 molar ratio, the reaction between **1** and IBr yields $\mathbf{1}{\cdot}IBr$ ($C_4H_7IBrNSSe$) microcrystals, whereas for a 1:2 molar ratio, violet crystals of formula $\mathbf{1}{\cdot}I_{1.25}Br_{0.75}$ ($C_4H_7I_{1.25}Br_{0.75}NSSe$; **II**), isotypic with those of **I**, have been obtained [space group *Cc*, with $a = 16.233(8)$ Å, $b = 5.900(4)$ Å, $c = 12.793(6)$ Å, $\beta = 127.43(3)°$, $Z = 4$, and $R = 0.038$]; here, the IBr molecule is bonded almost linearly [176.90(4)°] to the selenium atom through the iodine atom and about 25% of bromine is substituted by iodine thus obtaining a solid solution formed by 25% of the $\mathbf{1}{\cdot}I_2$ adduct and 75% of the $\mathbf{1}{\cdot}IBr$ adduct. The reaction of **2** with IBr yields both $\mathbf{2}{\cdot}IBr$ ($C_8H_7IBrNSSe$) microcrystals and $\mathbf{2}{\cdot}2IBr$ ($C_8H_7I_2Br_2NSSe$; **IV**) brown crystals using 1:1 and 1:2 molar ratios respectively. The crystals of **IV** are triclinic [space group $P\bar{1}$, with $a = 9.078(5)$ Å, $b = 9.872(5)$ Å, $c = 9.979(3)$ Å, $\alpha = 60.66(2)°$, $\beta = 74.21(2)°$, $\gamma = 82.09(2)°$, $Z = 2$, and $R = 0.027$]. On the basis of the large lengthening of the I−Br bond [3.129(1) Å] in the molecule coordinated to selenium, **IV** can be almost envisaged as an ionic $[2I]^+IBr_2^-$ compound, with the ions strongly interacting with each other. FT-Raman spectra of the solid samples are discussed compared with their structural features and with the spectra of CH_2Cl_2 solutions containing equimolecular concentrations of **1** (or **2**) and I_2 (or IBr). The strong Se−I bonds, obtained in all the reported compounds, indicate that these CT-complexes are different from those obtained from the sulfur compounds and that for the assignment of the infrared and Raman bands the three-body system Se•••I•••I(Br) should be better considered. A correlation between ν(I−Br) and *d*(I−Br) is also reported.

Introduction

In recent years, the great interest in the electric properties of solid polyiodide salts obtained by reacting diiodine with compounds having sulfur or selenium donor atoms[2] has encouraged our studies on the properties of solid compounds obtained by reacting diiodine and a great variety of pentaatomic rings. All the considered donors contained the thio- or selenoamido group, and the interaction with diiodine had been previously studied in CH_2Cl_2 solution.[3−6] On the whole, the results have shown that the stoichiometries of the solid complexes are often different from those found in solution, where 1:1 adducts are normally formed.[3−6] In particular, when one tries to crystallize solid CT complexes, several products can be prepared at least according to the following routes: (i) formation of neutral $D{\cdot}I_2$ CT-complexes, in which the diiodine binds the donor atom linearly;[3,5,7−19] (ii) formation, using diiodine concentrations

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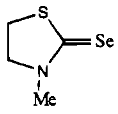
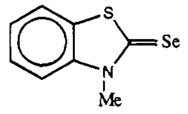
higher than 1:1 of D·nI$_2$ CT-complexes, in which the other diiodine molecules generally interact with the first bonded I_2[13,20–22] (a good example is one of the structures reported in the present paper); (iii) formation of two D–I terminal bonds by the homolitic break of I–I (see for example the hypervalent compounds of sulfur and selenium[12,23–25]); (iv) formation of iodonium salts, in which I^+ binds two donor molecules linearly, by the heterolitic break of coordinated I–I;[4,26–28] (v) reduction of iodine to polyiodides, by electron transfer from the donor to diiodine. No literature is reported here for the polyiodides, since by their variety (I^-, I_3^-, I_5^-, I_7^-, I_8^{2-}, I_{16}^{4-}, ...) and their structural features they are numberless.

Consequently, the great variety of products which can be obtained between donors and diiodine calls for other techniques for their identification, besides X-ray crystal structure determination. Raman spectroscopy has been widely used for this purpose, since it is known that it provides a simple way to obtain qualitative information about the molecular forms of polyiodides, and therefore it has been considered especially useful when single crystals suitable for X-ray diffractometric studies cannot be grown.[29–41] On the other hand, it had been shown[4,42] that, almost in the case of CT-complexes of weak or medium–weak strength, Raman spectroscopy can give information on the donor-diiodine bond interaction on the basis of the shift toward lower frequencies of the ν(I–I) Raman bands with respect to the value found in the solid I_2. However, it has also been shown that the ν(I-I) Raman bands of CT-complexes of weak or medium-weak strength fall in the same frequency region found for high polyiodides, which can be seen as CT-complexes between I^- or I_3^- with diiodine.[42–44] On the other hand, it is important to test the usefulness of Raman spectroscopy in the identification of other possible products obtainable in the solid state and, in particular, of strong adducts, in which I–I can no longer be considered a perturbed molecule. Thus, the synthesis and characterization by X-ray diffraction and Raman spectroscopy of strong adducts seems to be very important to correlate Raman bands with structural features.

Since CT-complexes of diiodine with selonic donors are generally very strong, we have reacted *N*-methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) and *N*-methylbenzothiazole-2(3*H*)-selone (**2**) with I_2 and IBr. **1** only yields the **1**·I_2 solid adduct both in the 1:1 and the 1:2 (donor/diiodine) molar ratios, whereas **2** produces the previously described $[\mathbf{2}_2\mathrm{I}]^+\mathrm{I}_3^-$ ionic compound[4] (1:1 molar ratio) and **2**·2I_2 (1:2 molar ratio). These results together with those obtained by reacting both donors with IBr in the same conditions used for I_2, as well as the discussion of the FT-Raman spectra recored in CH_2Cl_2 solution and on the solid compounds, are reported in the present paper.


(1)


(2)

Experimental Section

Materials. *N*-methylbenzothiazole-2(3*H*)-selone (**2**), diiodine, and iodine monobromide were purchased from Aldrich and used without further purification. *N*-Methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) was synthesized according to the procedure reported in ref 45.

***N*-Methyl-1,3-thiazolidine-2(3*H*)-selone–Diiodine (I).** This compound was obtained as black crystals with a violet metallic luster by evaporating a dichloromethane solution of *N*-methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) and diiodine both in 1:1 and 1:2 molar ratios in air at room temperature. Anal. Found (calcd for $C_4H_7I_2NSSe$): C, 11.10 (11.07); H, 1.61 (1.61); N, 3.33 (3.23); S, 7.51 (7.39).

***N*-Methyl-1,3-thiazolidine-2(3*H*)-selone–Iodine Monobromide (II).** This compound was obtained as yellow-orange microcrystals by evaporating a dichloromethane solution of *N*-methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) and iodine monobromide in a 1:1 molar ratio in air at room temperature. In the same conditions, but using a 1:2 (**1**/diiodine) molar ratio, violet crystals suitable for X-ray crystal structure determination have been obtained. From crystal data, this compound showed a composition corresponding to the empirical formula $C_4H_7I_{1.25}Br_{0.75}NSSe$ (**II**) (see Results). Anal. Found (calcd for $C_4H_7I_{1.25}Br_{0.75}NSSe$): C, 12.08 (12.03); H, 1.78 (1.77); N, 3.81 (3.51); S, 8.29 (8.03). The yellow-orange microcrystals, whose FT-Raman spectrum is reported in Figure 6, had the following analysis. Anal. Found (calcd for $C_4H_7IBrNSSe$):C, 12.58 (12.42); H, 1.83 (1.82); N, 3.65 (3.62); S, 8.61 (8.29).

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Table 1. Crystallographic Data

	1·I$_2$ (I)	**1·I$_{1.25}$Br$_{0.75}$ (II)**	**2·2I$_2$ (III)**	**2·2IBr (IV)**
formula	$C_4H_7I_2NSSe$	$C_4H_7I_{1.25}Br_{0.75}NSSe$	$C_8H_7I_4NSSe$	$C_8H_7I_2Br_2NSSe$
fw	433.94	398.68	735.79	641.80
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	*Cc*	*Cc*	$P\bar{1}$	$P\bar{1}$
a (Å)	16.400(7)	16.233(8)	11.439(4)	9.078(5)
b (Å)	5.976(3)	5.900(4)	14.337(4)	9.872(5)
c (Å)	12.942(4)	12.793(6)	16.479(6)	9.979(3)
α (deg)	90	90	115.47(2)	60.66(2)
β (deg)	127.66(2)	127.43(3)	97.02(3)	74.21(2)
γ (deg)	90	90	97.85(3)	82.09(2)
V (Å^3)	1004(1)	973(1)	2367(3)	750.1(6)
Z	4	4	6	2
ϱ_{calcd} (g cm^{-3})	2.870	2.722	3.097	2.841
μ(Mo Kα) (cm^{-1})	99.23	115.51	102.05	119.38
transm factors:				
ψ-scan	0.69−1.00	0.48−1.00	0.39−1.00	0.82−1.00
Difabs	0.67−1.20	0.72−1.25	0.82−1.18	0.79−1.24
no. of unique reflcns with $I > 3\sigma(I)$	854	968	5464	1494
final *R* and R_w indices[a]	0.024, 0.035	0.038, 0.048	0.028, 0.036	0.027, 0.035

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$. $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$.

***N*-Methylbenzothiazole-2(3*H*)-selone−Bis(diiodine) (III).** This compound was obtained as black crystals with metallic luster by evaporating a dichloromethane solution of *N*-methylbenzothiazole-2(3*H*)-selone (**2**) and diiodine in a 1:2 molar ratio in air at room temperature. Anal. Found (calcd for $C_8H_7I_4NSSe$): C, 13.10 (13.06); H, 0.90 (0.96); N, 1.95 (1.90); S, 4.40 (4.36).

***N*-Methylbenzothiazole-2(3*H*)-selone−Bis(iodine monobromide) (IV).** This compound was obtained as brown crystals by standing, for several days, a dichloromethane/benzene (60 ± 80 °C) (4/1 *v*/*v*) solution of *N*-methylbenzothiazole-2(3*H*)-selone (**2**) and iodine monobromide in a 1:2 molar ratio in air at 4 °C. Anal. Found (calcd for $C_8H_7I_2Br_2NSSe$): C, 15.19 (14.97); H, 1.00 (1.10); N, 2.50 (2.18); S, 5.20 (5.00).

***N*-Methylbenzothiazole-2(3*H*)-selone−Iodine Monobromide.** This compound was obtained as orange micro-crystals by standing a dichloromethane solution of *N*-methylbenzothiazole-2(3*H*)-selone (**2**) and iodine monobromide in a 1:1 molar ratio in air at room temperature for several days. Anal. Found (calcd for $C_8H_7IBrNSSe$): C, 22.24 (22.09); H, 1.66 (1.62); N, 3.37 (3.22); S, 7.28 (7.37).

FT-Raman and FT-IR Spectra. The FT Raman spectra were recorded by means of a Bruker FRS100 Fourier transform Raman spectrometer, operating with a diode-pumped Nd:YAG exciting laser emitting at 1064 nm wavelength and having a power impinging on the sample tunable up to 350 mW. The detection of the signal was made with an indium−gallium−arsenide detector operating at room temperature; all spectra were recorded at 4 cm^{-1} resolution, down to about 50 cm^{-1} Raman shift. The solid samples were packed into a suitable cell and then fitted into the compartment designed to use a 180° scattering geometry. The spectra in CH_2Cl_2 solution were recorded on solutions of **1** or **2** and I_2 (or IBr) in a 1:1 molar ratio, contained in a 0.5 cm path length quartz cell.

No sample decomposition was observed during the experiments. Only for the solution containing a 1:1 molar ratio of **2** and I_2, was a change in the spectrum with time observed; this was due to the precipitation of $[2_2I]^+I_3^-$ (see Discussion).

The infrared spectra were recorded by means of a Bruker IFS66 Fourier transform infrared spectrometer on polyethylene pellets in the 500−80 cm^{-1} range.

X-ray Data Collection and Structure Determination. Crystal data and other experimental details are summarized in Table 1. The crystals used were coated with cyanoacrilate glue in order to prevent decomposition due to loss of diodine or IBr during data collection. The diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo *K*α radiation (λ = 0.710 73 Å). The unit-cell parameters and an orientation matrix were obtained by a least-squares fit of 25 randomly oriented intense reflections. The diffracted intensities were collected using a variable scan speed. Three standard reflections were measured at regular intervals and showed no decay of the scattering power of the crystal during data collection, with the exception of compound **IV**, for which the decay at the end of the data collection was ca. 32% on F_o. The intensities were corrected for Lorentz and polarization effects, decay, as well as absorption. The absorption correction was applied according to the procedure described in Demartin *et al.*,[46] *i.e.* by performing a ψ-scan correction[47] followed by a DIFABS correction.[48] Secondary extinction correction was applied, with the exception of the data for **IV**, in the form $|F_c|/1 + gIc$ with $g = 4.56 \times 10^{-7}$ for **I**, 2.01×10^{-7} for **II**, and 1.14×10^{-7} for **III**. Scattering factors for all the atomic species and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from ref 49. All structures were solved by direct methods (MULTAN)[50] and refined by full-matrix least-squares methods, minimizing the function $\Sigma w(|F_o| - k|F_c|)^2$. Individual weights were assigned as $w = 1/\sigma^2(F_o)$. For the noncentrosymmetric **1**·I_2, two independent refinements allowed the correct enantiomorph to be established, whose atomic coordinates are reported in Table 3; the rejected enantiomorph gave significantly higher *R* and R_w indices (0.025 and 0.037, respectively). The same refinement test carried out on both enantiomorphs of compound **II** was not significant.

An anisotropic thermal parameter was assigned to all the non-hydrogen atoms. For **II**, the occupancy of the I and Br atoms was also refined to account for a non negligible amount (about 25%) of **I** co-crystallized, whose presence was suggested by an anomalous thermal parameter of the Br atom (see also the preparation of **II** and the discussion of FT-Raman spectra). The final difference Fourier syntheses in all cases showed maxima residuals close to the halogen atoms. All calculations were performed on a PDP 11/73 computer using the SDP-Plus structure determination package.[51]

Results

All the compounds obtained by reacting **1** and **2** with diiodine and IBr in dichlorometane solution in 1:1 and 1:2 molar ratios are summarized in Table 2. With I_2, **1** yields only a 1:1 adduct both with 1:1 and 1:2 molar ratios. The reaction of **1** with IBr yields adducts with variable content of iodine and bromine depending on the donor/IBr molar ratio; the crystal used for the X-ray crystal structure determination had formula **1**·$I_{1.25}$-

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Table 2. All the Compounds Obtained by Reacting **1** and **2** with I_2 and IBr (1:1 and 1:2 Molar Ratios) in CH_2Cl_2 Solution

	D:I_2(IBr) ratio	**1**	**2**
I_2	1:1	**1**·I_2 (**I**) adduct	[$\mathbf{2}_2$I]$^+I_3^-$ ionic compd
	1:2	**1**·I_2 (**I**) adduct	**2**·2I_2 (**III**) adduct
IBr	1:1	**1**·IBr adduct	**2**·IBr adduct
	1:2	**1**·$I_{1+x}Br_{1-x}$ (**II**) adduct^a	[**2**I]$^+IBr_2^-$ (**IV**) ionic compd

^{a} $x = 0.25$ for the crystals used for X-ray crystal structure determination.

Table 3. Fractional Atomic Coordinates and Thermal Parameters of Non-Hydrogen Atoms (Esd's in Parentheses) for **1**·I_2 (**I**)

atom	x	y	z	B_{eq} (Å^2)^a
I(1)	1.000	0.7980(1)	1.000	3.58(1)
I(2)	1.08639(5)	1.0834(1)	0.89880(6)	4.33(1)
Se	0.92758(6)	0.5444(2)	1.10316(8)	4.20(2)
S	0.7975(2)	0.4051(5)	0.8031(2)	4.50(6)
N(1)	0.7915(5)	0.193(1)	0.9691(6)	3.3(2)
C(1)	0.8361(6)	0.362(1)	0.9579(7)	3.1(2)
C(2)	0.7151(8)	0.070(2)	0.845(1)	4.3(3)
C(3)	0.697(1)	0.198(3)	0.7381(9)	6.7(3)
C(4)	0.8089(7)	0.128(2)	1.0899(8)	4.1(2)

^{a} $B_{eq} = {}^4/_3\,[a^2\beta(1,1) + b^2\beta(2.2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 4. Fractional Atomic Coordinates and Thermal Parameters of Non-Hydrogen Atoms (Esd's in Parentheses) for **1**·$I_{1.25}Br_{0.75}$ (**II**)

atom	x	y	z	B_{eq}(Å^2)^a
I	1.000	0.8017(2)	1.000	4.13(2)
Br	1.08575(8)	1.0837(2)	0.90097(9)	4.79(2)
Se	0.92869(9)	0.5495(3)	1.1047(1)	4.67(3)
S	0.7945(3)	0.4067(7)	0.8013(3)	5.13(9)
N(1)	0.7894(7)	0.195(2)	0.9705(7)	3.8(2)
C(1)	0.8347(7)	0.361(2)	0.9574(9)	3.6(2)
C(2)	0.712(1)	0.071(2)	0.852(1)	4.7(4)
C(3)	0.696(2)	0.199(4)	0.737(1)	7.7(6)
C(4)	0.806(1)	0.127(3)	1.092(1)	5.1(3)

^{a} See footnote in Table 3.

Table 5. Fractional Atomic Coordinates and Thermal Parameters of Non-Hydrogen Atoms (Esd's in Parentheses) for **2**·2I_2 (**III**)

atom	x	y	z	B_{eq} (Å^2)^a
I(11)	0.26922(5)	0.24659(4)	0.12292(3)	3.56(1)
I(12)	0.50517(5)	0.34958(4)	0.09596(4)	4.11(1)
I(13)	0.33974(4)	0.37859(4)	−0.05571(3)	3.47(1)
I(14)	0.19103(6)	0.39815(5)	−0.18899(4)	4.65(2)
I(21)	0.04714(5)	0.45813(4)	0.25812(4)	3.46(1)
I(22)	−0.17589(5)	0.38609(5)	0.31858(4)	5.01(2)
I(23)	−0.33223(6)	0.13831(5)	0.19090(4)	5.62(2)
I(24)	−0.43689(5)	−0.07199(5)	0.07829(4)	5.17(2)
I(31)	0.63482(5)	0.06773(4)	0.44930(3)	3.41(1)
I(32)	0.76372(6)	−0.08864(5)	0.33330(4)	4.99(2)
I(33)	0.08043(5)	0.17788(5)	0.53700(4)	5.23(2)
I(34)	1.03681(6)	−0.26250(6)	0.56343(5)	5.89(2)
Se(11)	0.07212(8)	0.16267(7)	0.15633(6)	4.30(2)
Se(21)	0.23903(8)	0.51829(7)	0.20197(6)	4.16(2)
Se(31)	0.49201(8)	0.18628(6)	0.55238(6)	4.04(2)
S(11)	0.2081(2)	−0.0194(2)	0.0518(1)	3.75(5)
S(21)	0.1334(2)	0.7222(2)	0.3026(1)	3.35(5)
S(31)	0.6763(2)	0.3506(2)	0.5242(1)	3.64(5)
N(11)	0.0264(5)	−0.0528(5)	0.1174(4)	3.4(1)
N(21)	0.3096(5)	0.7248(5)	0.2225(4)	3.2(1)
N(31)	0.5014(5)	0.4018(5)	0.6031(4)	2.8(1)
C(11)	0.0590(7)	−0.1497(6)	0.0795(5)	3.4(2)
C(12)	0.0059(8)	−0.2414(7)	0.0804(6)	5.0(2)
C(13)	0.053(1)	−0.3289(7)	0.0389(7)	5.9(3)
C(14)	0.150(1)	−0.3271(7)	−0.0019(7)	5.7(3)
C(15)	0.2057(8)	−0.2362(8)	−0.0031(6)	5.0(3)
C(16)	0.1585(7)	−0.1463(6)	0.0389(5)	3.4(2)
C(17)	0.0955(6)	0.0253(6)	0.1101(5)	3.2(2)
C(18)	−0.0768(7)	−0.0346(7)	0.1660(6)	5.3(2)
C(21)	0.2892(7)	0.8282(6)	0.2560(5)	3.1(2)
C(22)	0.3511(8)	0.9125(7)	0.2468(6)	4.3(2)
C(23)	0.3139(9)	1.0055(7)	0.2831(6)	5.0(2)
C(24)	0.2187(9)	1.0174(6)	0.3267(6)	5.0(3)
C(25)	0.1570(8)	0.9364(7)	0.3379(6)	4.3(2)
C(26)	0.1933(6)	0.8397(6)	0.3010(5)	3.0(2)
C(27)	0.2341(6)	0.6602(6)	0.2410(5)	3.0(2)
C(28)	0.4089(7)	0.6950(7)	0.1726(6)	4.5(2)
C(31)	0.5600(6)	0.4961(5)	0.6057(5)	2.8(2)
C(32)	0.5263(7)	0.5925(6)	0.6411(5)	3.6(2)
C(33)	0.5925(8)	0.6750(6)	0.6323(6)	4.1(2)
C(34)	0.6947(8)	0.6599(6)	0.5932(6)	4.2(2)
C(35)	0.7297(7)	0.5636(7)	0.5582(5)	4.4(2)
C(36)	0.6599(7)	0.4804(6)	0.5637(5)	3.1(2)
C(37)	0.5515(7)	0.3192(6)	0.5636(5)	3.3(2)
C(38)	0.3976(7)	0.3975(7)	0.6464(6)	4.3(2)

^{a} See footnote in Table 3.

$Br_{0.75}$ (**II**). **2** yields compounds having both stoichiometries **2**·I_2(IBr) and **2**·2I_2(IBr). All the compounds, except **2**·IBr, have been suitable for X-ray crystal structure determination.

Crystal Structures of 1·I_2 (I) and 1·$I_{1.25}Br_{0.75}$ (II). The fractional atomic coordinates of compounds **I** and **II** are reported in Tables 3 and 4, respectively; selected interatomic distances and angles are shown in Table 7. Both compounds are isotypic (see Table 1) and the monoclinic unit cell contains four molecular adducts, in which selenium binds almost linearly the iodine atom of I_2 [177.49(3)°] and that of IBr [176.90(4)°] respectively (Figure 1). The I−I bond order of 0.43, calculated according to Pauling equation,[52] indicates a strong interaction of the diodine molecule with the selenium atom. In the crystals of **I** the shortest intermolecular I···I contact is 4.496(1) Å and the other contacts among the different units are normal van der Waals interactions. The Se−I bond becomes stronger [d(Se−I) = 2.689(1) Å] in **II**, according to the increased acidic properties of IBr with respect to I_2. Correspondingly, the I−Br distance of 2.908(1) Å is very large compared to those found for the analogous CT-complexes with sulfur donors, i.e. 1,4-dithiacycloexane·2IBr [d(I−Br) = 2.646(1) Å][53] and 5,5-dimethyl-2-thioxo-4-one·IBr [d(I-Br) = 2.738(1) Å],[54] and in the IBr_2^- anions, reported in the literature.[55−68] As reported in the Experimental Section, the X-ray crystal structure indicates that the exact formulation of this compound is $C_4H_7I_{1.25}Br_{0.75}NSSe$,

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(52) The equation proposed by Pauling for the calculation of the I−I bond order is $d = d_0 - c \log \mathbf{n}$ [where d and d_0 (2.67 Å) are the bond distances of coordinated and free I_2, c (0.85 Å) is an empirical constant, and **n** is the bond order]: Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

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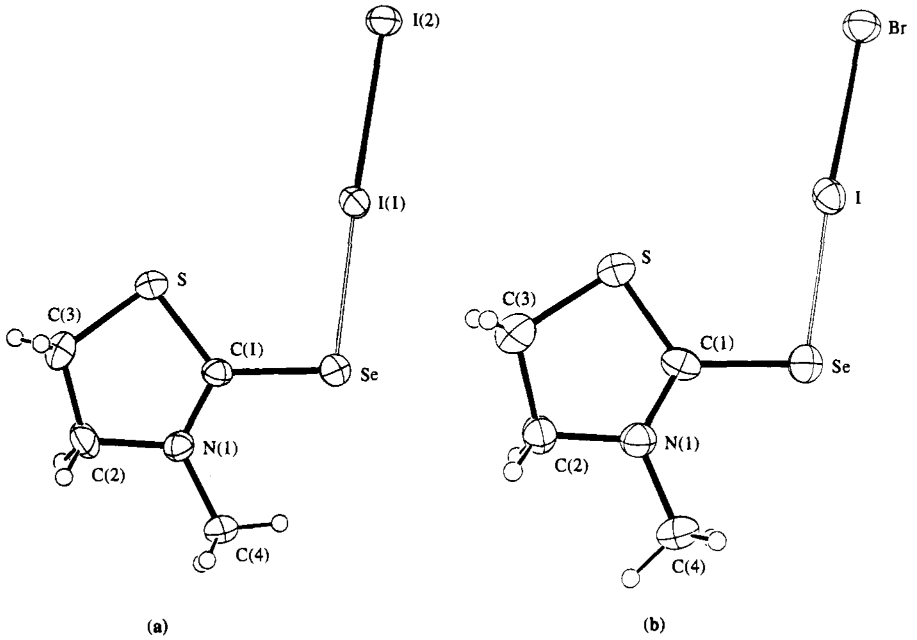

Figure 1. ORTEP drawing of $1{\cdot}I_2$ (**I**) (a) and $1{\cdot}I_{1.25}Br_{0.75}$ (**II**) (b).

also in accordance with the analytical data and with the FT-Raman spectrum. Recently, dealing with adducts of tertiary phosphines with IBr, McAuliffe et al.[69] have reported the X-ray crystal structure of Ph_3PIBr, recrystallized from diethyl ether/1,2-dichloroethane (1:1). In that case also, the crystal used for the X-ray analysis was rich in iodine, with an empirical formula $Ph_3PI_{1.29}Br_{0.71}$. The I−Br bond distance in that case was 3.062(2) Å, that is higher than in our case. However, in **II** the coordination of IBr through the bromine atom can be ruled out on the basis of the occupancy refinement for the I atom, which is not significantly different from 1.00, whereas the $Ph_3PI_{1.29}Br_{0.71}$ the authors calculated that the halogen atom bound directly to the phosphorus atom was 86(2)% I and 14(2)% Br.

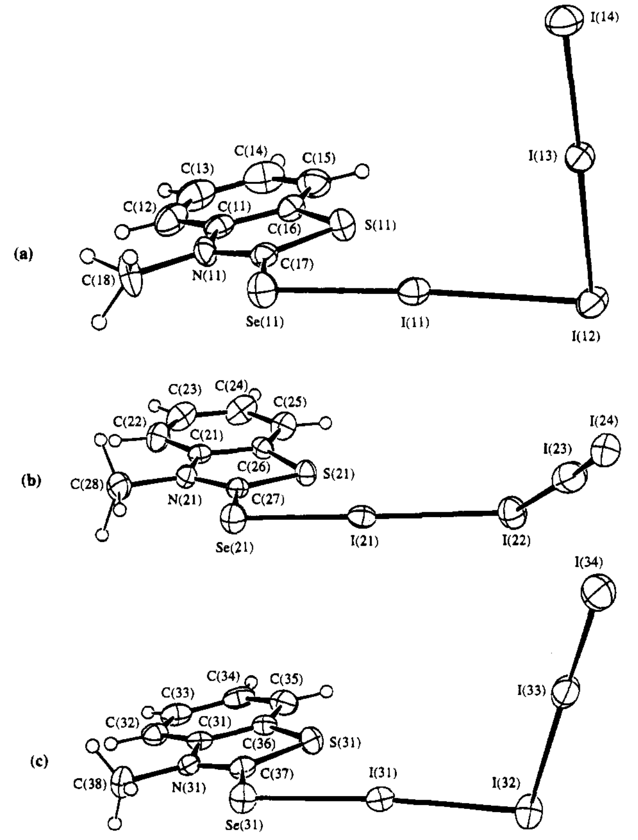

Figure 2. ORTEP drawing of the three independent molecular adducts in $2{\cdot}2I_2$ (**III**).

Crystal Structure of $2{\cdot}2I_2$ (III). The fractional atomic coordinates of compound **III** are reported in Table 5; selected interatomic distances and angles are shown in Table 8a. The triclinic unit-cell contains six molecular adducts with formula $2{\cdot}2I_2$, three of which are independent (the asymmetric unit) while the other three are related to the former by inversion. Perspective views of each adduct, obtained maintaining the same orientation of the organic molecule, are shown in parts a−c of Figure 2; from these pictures it is evident that every adduct differs from the others in the arrangement of the diodine molecule not directly bonded to the organic moiety. Such a different conformational situation can be better understood on examining the whole packing of the adduct molecules in the crystal lattice, which is shown in Figure 3. The organic molecules are arranged on parallel stacked planes separated by "graphite-like" interactions. The diodine molecule directly bound to the selenium atom lies essentially on these planes. The second diodine molecule, instead, fits into the cavities left between the *N*-methylbenzothiazole-2(3*H*)-selone·I_2 sheets. The pattern of the I−I distances clearly shows a noteworthy reduction of the bond order[52] in the molecules directly bonded to Se with I−I distances in the range 2.960(1)−3.071(1) Å, the longest I−I distance corresponding to the shortest Se−I [range of the Se−I distances 2.639(1)−2.720(1) Å]. The range of I−I distances for the diodine molecules not bonded to Se is 2.746(1)−2.764(1) Å, consistent with the values observed for weakly perturbed diodine molecules. Intramolecular interactions between the diodine molecules range from 3.155(1) to 3.380(1) Å. The shortest intermolecular I···I contacts are I(22)···I(34) [3.525(1) Å] and I(12)···I(24) [3.670(1) Å], thus defining a kind

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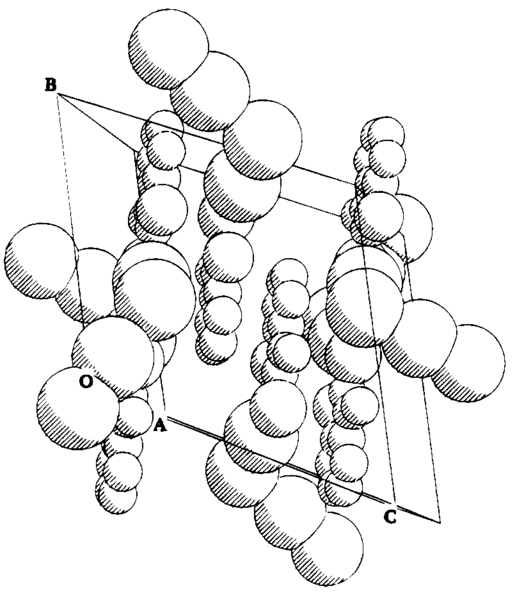

Figure 3. Crystal packing of $\mathbf{2}\cdot2\mathrm{I}_2$ (**III**) obtained with PLUTO.

Table 6. Fractional Atomic Coordinates and Thermal Parameters of Non-Hydrogen Atoms (Esd's in Parentheses) for $\mathbf{2}\cdot2\mathrm{IBr}$ (**IV**)

atom	x	y	z	B_{eq} (Å^2)[a]
I(1)	0.13714(7)	0.18003(6)	0.90499(7)	3.98(2)
I(2)	−0.12676(7)	0.19570(6)	0.61425(6)	3.64(2)
Br(1)	0.1626(1)	0.0667(1)	0.6565(1)	4.39(3)
Br(2)	−0.4031(1)	0.3188(1)	0.5957(1)	4.95(3)
Se(1)	0.0887(1)	0.2635(1)	1.1196(1)	4.01(3)
S(1)	0.3083(3)	0.5114(2)	0.8093(2)	3.45(6)
N(1)	0.2478(9)	0.5158(7)	1.0703(8)	3.5(2)
C(1)	0.342(1)	0.6468(9)	0.9649(9)	3.1(2)
C(2)	0.393(1)	0.7516(9)	0.998(1)	3.6(2)
C(3)	0.489(1)	0.8663(9)	0.876(1)	4.4(3)
C(4)	0.539(1)	0.8773(9)	0.726(1)	3.7(3)
C(5)	0.489(1)	0.7748(9)	0.6927(9)	3.3(2)
C(6)	0.3885(9)	0.6599(8)	0.8148(9)	2.7(2)
C(7)	0.218(1)	0.4372(9)	1.0056(9)	3.1(2)
C(8)	0.183(1)	0.477(1)	1.240(1)	4.7(3)

[a] See footnote in Table 3.

of "trimeric aggregate" of $\mathbf{2}\cdot2\mathrm{I}_2$ adducts, the remaining short interactions ranging from 3.970(1) to 4.470(1) Å.

Crystal Structure of $\mathbf{2}\cdot2\mathrm{IBr}$ (IV). The fractional atomic coordinates of compound **IV** are reported in Table 6; selected interatomic distances and angles are shown in Table 8b. **IV** can be considered as a linear adduct $\mathbf{2}\cdot\mathrm{IBr}$ [Se(1)−I(1)−Br(1) 174.32(4)°] interacting with a second IBr molecule [Br(1)−I(2)−Br(2) 175.38(4)°] (see Figure 4). However, on the basis of the very large lengthening of the IBr bond [3.129(1) Å] of the molecule coordinated with selenium, $\mathbf{2}\cdot2\mathrm{IBr}$ should be better considered an ionic $[\mathbf{2}\mathrm{I}]^+\mathrm{IBr}_2^-$ compound, with the ions strongly interacting with each other. This view is confirmed by the bond distances obtained in the anion, Br(1)−I(2) and I(2)−Br(2), 2.803(1) and 2.645(1) Å, respectively, which can be considered as an asymmetric IBr_2^- anion. On the other hand, also the Se−I bond distance of 2.564(1) Å, which is shorter than the analogous bond distances found in the present and in previously reported structures with interhalogens,[3,15−18,70] but similar to that found in 2,4,6-tri-*tert*-butylphenyl(iodo)selenide (2.529 Å),[71] should support the ionic formulation. The crystal packing in Figure 5 shows that the IBr_2^- anions are normal to the $[\mathbf{2}\mathrm{I}]^+$ molecular planes [the I(1)−Br(1)−I(2) angle is 89.27(3)°].

Table 7. Selected Interatomic Distances (Å) and Angles (deg)[a]

	(a) Compound $\mathbf{1}\cdot\mathrm{I}_2$ (**I**)		
I(1)−I(2)	2.983(1)	N(1)−C(1)	1.306(10)
I(1)−Se	2.726(1)	N(1)−C(2)	1.493(11)
Se−C(1)	1.877(8)	N(1)−C(4)	1.460(11)
S−C(1)	1.712(8)	C(2)−C(3)	1.449(15)
S−C(3)	1.802(12)	I(1)···I(2)^i	4.496(1)
I(2)−I(1)−Se	177.49(3)	Se−C(1)−S	125.6(4)
I(1)−Se−C(1)	98.8(2)	Se−C(1)−N(1)	119.8(6)
C(1)−S−C(3)	91.3(5)	S−C(1)−N(1)	114.4(6)
C(1)−N(1)−C(2)	115.0(7)	N(1)−C(2)−C(3)	108.2(7)
C(1)−N(1)−C(4)	124.6(7)	S−C(3)−C(2)	108.9(7)
C(2)−N(1)−C(4)	120.4(8)		
	(b) Compound $\mathbf{1}\cdot\mathrm{I}_{1.25}\mathrm{Br}_{0.75}$ (**II**)		
I−Br	2.908(1)	N(1)−C(1)	1.295(14)
I−Se	2.689(1)	N(1)−C(2)	1.449(14)
Se−C(1)	1.902(11)	N(1)−C(4)	1.469(14)
S−C(1)	1.703(10)	C(2)−C(3)	1.522(18)
S−C(3)	1.771(18)	I···Br^i	4.476(1)
Br−I−Se	176.90(4)	Se−C(1)−S	125.1(6)
I−Se−C(1)	99.1(3)	Se−C(1)−N(1)	119.4(8)
C(1)−S−C(3)	91.8(6)	S−C(1)−N(1)	115.3(8)
C(1)−N(1)−C(2)	116.1(9)	N(1)−C(2)−C(3)	107.3(10)
C(1)−N(1)−C(4)	126.4(10)	S−C(3)−C(2)	108.3(9)
C(2)−N(1)−C(4)	117.4(10)		

[a] Symmetry code: (*i*) x, $2 - y$, $z + 1/2$.

FT-IR and FT-Raman Spectra. FT-IR and FT-Raman bands (cm^{-1}) of the solid samples of all compounds reported in this paper are collected in Table 9. As one can see, there is a good correspondence between the infrared and the Raman spectra. The FT-IR and FT-Raman bands of **IV** are also reported in Table 10 together with those of the other IBr_2^- ions reported in literature.[55,72−74] The spectra in solution have been recorded only for the 1:1 molar ratio between **1** (or **2**) and I_2 (or IBr), since a greater dihalogen content increases only its free peak. The maximum concentrations that can be obtained for **1** with I_2 and IBr are about 10^{-2} M and 5×10^{-3} M respectively, without forming a precipitate. In these conditions, the solution containing $\mathbf{1}\cdot\mathrm{I}_2$ shows two very small and broad peaks at 117 and 139 cm^{-1}, while that of $\mathbf{1}\cdot\mathrm{IBr}$ shows only a very small peak at 150 cm^{-1}. For **2** it has been possible to obtain solutions with higher concentrations (ca. 3.5×10^{-2} M); the solution containing $\mathbf{2}\cdot\mathrm{I}_2$ shows two broad peaks at 108 and 139 cm^{-1}, and that of $\mathbf{2}\cdot\mathrm{IBr}$ two broad peaks at 123 and 160 cm^{-1}. Only the spectrum of the solution containing $\mathbf{2}\cdot\mathrm{I}_2$ changes with the time, as a consequence of the precipitation of $[\mathbf{2}_2\mathrm{I}]^+\mathrm{I}_3^-$ (see Discussion).

Discussion

The reaction of *N*-methylbenzothiazole-2(3*H*)-selone (**2**) with diiodine in a 1:1 molar ratio yields the $[\mathbf{2}_2\mathrm{I}]^+\mathrm{I}_3^-$ iodonium salt, which is the first example reported in literature of iodonium salt with a selenium donor atom.[4] On the other hand, the reaction of the sulfur isologue compound, i.e. *N*-methylbenzothiazole-2(3*H*)-thione, with diiodine in a 1:2 molar ratio yields an iodonium salt, whose counterion is a heptaiodide describable as $\mathrm{I}^-\cdot3\mathrm{I}_2$, having a symmetry very close to C_{3v}.[4] Thus, it could be foreseen that from the reaction of **2** with diiodine in a 1:2 molar ratio a new heptaiodide could be obtained. Unexpectedly,

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Table 8. Selected Interatomic Distances (Å) and Angles (deg)

		(a) Compound **2**·2I$_2$ (**III**)^{a}			
I(11)–I(12)	3.071(1)	N(21)–C(21)	1.407(9)	I(11)···I(13)	4.225(1)
I(11)–Se(11)	2.639(1)	N(21)–C(27)	1.336(9)	I(11)···I(21)	4.277(1)
I(12)–I(13)	3.155(1)	N(21)–C(28)	1.486(9)	I(11)···I(24)^{i}	4.082(1)
I(13)–I(14)	2.746(1)	N(31)–C(31)	1.406(9)	I(12)···I(13)^{ii}	4.404(1)
I(21)–I(22)	3.059(1)	N(31)–C(37)	1.330(9)	I(12)···I(14)^{ii}	4.243(1)
I(21)–Se(21)	2.662(1)	N(31)–C(38)	1.465(9)	I(12)···I(23)^{iii}	4.470(1)
I(22)–I(23)	3.341(1)	C(11)–C(12)	1.377(11)	I(12)···I(24)^{i}	3.670(1)
I(23)–I(24)	2.762(1)	C(11)–C(16)	1.394(10)	I(13)···I(13)^{ii}	4.278(1)
I(31)–I(32)	2.960(1)	C(12)–C(13)	1.366(14)	I(14)···I(21)^{iv}	3.970(1)
I(31)–Se(31)	2.720(1)	C(13)–C(14)	1.373(14)	I(14)···I(22)^{iv}	4.461(1)
I(32)–I(33)	3.380(1)	C(14)–C(15)	1.379(13)	I(14)···I(32)^{v}	4.179(1)
I(33)–I(34)	2.764(1)	C(15)–C(16)	1.395(11)	I(14)···I(33)^{v}	4.148(1)
Se(11)–C(17)	1.853(8)	C(21)–C(22)	1.390(11)	I(22)···I(34)^{vii}	3.525(1)
Se(21)–C(27)	1.864(8)	C(21)–C(26)	1.387(9)	I(23)···I(34)^{vii}	4.449(1)
Se(31)–C(37)	1.855(8)	C(22)–C(23)	1.360(12)	I(24)···I(24)^{viii}	4.182(1)
S(11)–C(16)	1.742(8)	C(23)–C(24)	1.366(12)	I(31)···I(31)^{vii}	4.300(1)
S(11)–C(17)	1.730(7)	C(24)–C(25)	1.369(11)	I(31)···I(34)^{vi}	4.448(1)
S(21)–C(26)	1.743(7)	C(25)–C(26)	1.398(11)		
S(21)–C(27)	1.713(7)	C(31)–C(32)	1.380(10)		
S(31)–C(36)	1.734(8)	C(31)–C(36)	1.402(10)		
S(31)–C(37)	1.721(7)	C(32)–C(33)	1.386(11)		
N(11)–C(11)	1.384(10)	C(33)–C(34)	1.401(12)		
N(11)–C(17)	1.337(9)	C(34)–C(35)	1.386(12)		
N(11)–C(18)	1.496(9)	C(35)–C(36)	1.384(10)		
I(12)–I(11)–Se(11)	176.66(3)	N(11)–C(11)–C(12)	127.2(8)	Se(21)–C(27)–N(21)	122.7(5)
I(11)–I(12)–I(13)	85.46(2)	N(11)–C(11)–C(16)	111.9(6)	S(21)–C(27)–N(21)	112.6(6)
I(12)–I(13)–I(14)	178.25(3)	C(12)–C(11)–C(16)	121.0(8)	N(31)–C(31)–C(32)	127.0(7)
I(22)–I(21)–Se(21)	178.84(3)	C(11)–C(12)–C(13)	117.7(9)	N(31)–C(31)–C(36)	110.8(6)
I(21)–I(22)–I(23)	117.99(2)	C(12)–C(13)–C(14)	122.0(9)	C(32)–C(31)–C(36)	122.1(7)
I(22)–I(23)–I(24)	173.27(3)	C(13)–C(14)–C(15)	121.4(9)	C(31)–C(32)–C(33)	118.3(7)
I(32)–I(31)–Se(31)	171.52(3)	C(14)–C(15)–C(16)	117.0(8)	C(32)–C(33)–C(34)	119.3(8)
I(31)–I(32)–I(33)	108.99(2)	S(11)–C(16)–C(11)	110.3(6)	C(33)–C(34)–C(35)	122.7(7)
I(32)–I(33)–I(34)	176.48(3)	S(11)–C(16)–C(15)	128.9(6)	C(34)–C(35)–C(36)	117.5(7)
I(11)–Se(11)–C(17)	97.4(2)	C(11)–C(16)–C(15)	120.8(7)	S(31)–C(36)–C(31)	110.9(5)
I(21)–Se(21)–C(27)	99.6(2)	Se(11)–C(17)–S(11)	124.9(4)	S(31)–C(36)–C(35)	129.0(6)
I(31)–Se(31)–C(37)	102.3(2)	Se(11)–C(17)–N(11)	124.0(5)	C(31)–C(36)–C(35)	120.0(7)
C(16)–S(11)–C(17)	91.2(4)	S(11)–C(17)–N(11)	111.0(6)	Se(31)–C(37)–S(31)	124.6(5)
C(26)–S(21)–C(27)	90.9(3)	N(21)–C(21)–C(22)	127.7(7)	Se(31)–C(37)–N(31)	123.4(5)
C(36)–S(31)–C(37)	91.2(4)	N(21)–C(21)–C(26)	111.7(6)	S(31)–C(37)–N(31)	112.0(5)
C(11)–N(11)–C(17)	115.5(6)	C(22)–C(21)–C(26)	120.6(7)		
C(11)–N(11)–C(18)	122.7(6)	C(21)–C(22)–C(23)	117.7(8)		
C(17)–N(11)–C(18)	121.7(7)	C(22)–C(23)–C(24)	122.2(8)		
C(21)–N(21)–C(27)	114.0(6)	C(23)–C(24)–C(25)	121.6(8)		
C(21)–N(21)–C(28)	120.8(6)	C(24)–C(25)–C(26)	117.4(7)		
C(27)–N(21)–C(28)	125.3(7)	S(21)–C(26)–C(21)	110.7(5)		
C(31)–N(31)–C(37)	115.0(6)	S(21)–C(26)–C(25)	128.6(6)		
C(31)–N(31)–C(38)	122.0(6)	C(21)–C(26)–C(25)	120.6(7)		
C(37)–N(31)–C(38)	122.9(6)	Se(21)–C(27)–S(21)	124.7(4)		
		(b) Compound **2**·2IBr (**IV**)^{b}			
I(1)–Br(1)	3.129(1)	N(1)–C(1)	1.413(10)	C(4)–C(5)	1.373(12)
I(1)–Se(1)	2.564(1)	N(1)–C(7)	1.317(10)	C(5)–C(6)	1.390(11)
I(2)–Br(1)	2.803(1)	N(1)–C(8)	1.497(14)	I(1)···I(1)^{i}	3.961(1)
I(2)–Br(2)	2.645(1)	C(1)–C(2)	1.390(12)	I(2)···Se(1)^{i}	3.999(1)
Se(1)–C(7)	1.880(8)	C(1)–C(6)	1.386(11)	Br(1)···Se(1)^{i}	3.600(1)
S(1)–C(6)	1.754(8)	C(2)–C(3)	1.367(12)	Br(2)···Br(2)^{ii}	3.598(2)
S(1)–C(7)	1.711(8)	C(3)–C(4)	1.392(13)		
Br(1)–I(1)–Se(1)	174.32(4)	C(7)–N(1)–C(8)	123.9(10)	C(4)–C(5)–C(6)	117.0(9)
Br(1)–I(2)–Br(2)	175.38(4)	N(1)–C(1)–C(2)	128.0(8)	S(1)–C(6)–C(1)	110.6(6)
I(1)–Br(1)–I(2)	89.27(3)	N(1)–C(1)–C(6)	111.2(7)	S(1)–C(6)–C(5)	127.6(7)
I(1)–Se(1)–C(7)	97.8(3)	C(2)–C(1)–C(6)	120.8(7)	C(1)–C(6)–C(5)	121.8(8)
C(6)–S(1)–C(7)	90.7(4)	C(1)–C(2)–C(3)	117.0(9)	Se(1)–C(7)–S(1)	124.5(5)
C(1)–N(1)–C(7)	114.7(7)	C(2)–C(3)–C(4)	122.4(10)	Se(1)–C(7)–N(1)	122.6(6)
C(1)–N(1)–C(8)	121.4(10)	C(3)–C(4)–C(5)	120.9(10)	S(1)–C(7)–N(1)	112.9(6)

[a] Symmetry codes for part a: (*i*) −*x*, −*y*, −*z*; (*ii*) 1 − *x*, 1 − *y*, − *z*; (*iii*) 1 + *x*, *y*, *z*; (*iv*) −*x*, 1 − *y*, −*z*; (*v*) 1 − *x*, −*y*, −*z*; (*vi*) 2 − *x*, −*y*, 1 − *z*; (*vii*) 1 − *x*, −*y*, 1 − *z*; (*viii*) −1 − *x*, −*y*, −*z*. [b] Symmetry codes for part b: (*i*) −*x*, −*y*, 2 − *z*; (*ii*) −1 − *x*, 1 − *y*, 1 − *z*.

by reacting **2** and diiodine in a 1:2 molar ratio, the described neutral adduct of formula **2**·2I$_2$ (**III**) was obtained as crystals. Two features of the structure of **III** must be pointed out: (i) the arrangement of the organic molecules on parallel stacked planes separated by "graphite-like" interactions and (ii) the identification of trimeric aggregates interacting with each other by contacts higher than 3.970(1) Å. Within the trimeric aggregate, all the I··I contacts are shorter than 3.670(1) Å, thus defining a chain of twelve iodine atoms anchored by three selenium atoms.

Although oligomeric chains of iodine and iodide moieties are quite common, oligomeric poliiodine cations[75] and chains

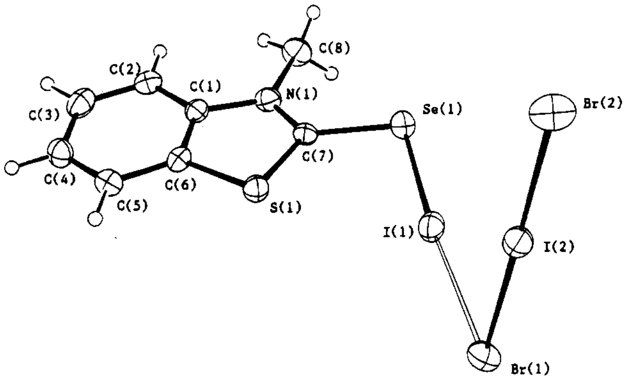

Figure 4. ORTEP drawing of 2·2IBr (IV).

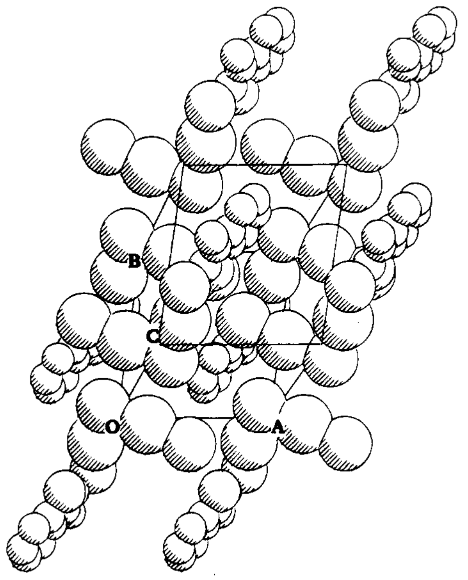

Figure 5. Crystal packing of 2·2IBr (IV) obtained with PLUTO.

of neutral diiodine molecules are less so.[13,20-22] Among the neutral diiodine chains reported in literature, bis(triphenylphosphane sulfide diiodine) diiodine shows an $(I_2)_3$-chain anchored at its two ends by sulfur atoms,[21,22] whereas, on the basis of structural data, the $(I_2)_7$-chain of bis(dithizone)heptakis(diiodine) has been described by the authors[13,20] as a sequence of $C{=}S\cdots I\cdots[I_5]^-\cdots I_2\cdots[I_5]^-\cdots I\cdots S{=}C$ atoms and not properly as a chain of neutral diiodine molecules. In spite of its wide network of diiodine molecules, the electric conductivity of **III** is very low, considering the large I··I contacts between the trimeric aggregates. As found for the sulfur-diiodine interaction,[3,13] the Se··I··I arrangement is also essentially linear and the values of d(Se··I) are correlated with those of d(I··I). This correlation might fit the equation of a hyperbola (Figure 7), as in sulfur complexes, but a confirmation of this should be obtained by preparing complexes having a greater asymmetry in the Se··I··I arrangement. In contrast with the adducts with sulfur donors, which can generally be considered of weak or medium–weak strength,[42,44] in the selenium isologues the Se··I_2 interaction is far stronger, as is proved by the noteworthy lengthening of the I··I bond distances. In the presence case, in fact, the I··I bond order values, calculated according to Pauling,[52] become 0.34, 0.35, and 0.46 for the three Se-bonded diiodine molecules.

A comparison between the structures of **III** and **IV** shows that the arrangement of the two IBr molecules is similar to that found for the two diiodine molecules in each asymmetric unit of **III**. However, as pointed out in the Results, the Se–I bond in **IV** is stronger [d(Se··I) = 2.564(1) Å] than that found in **III** and it is only 0.035 Å longer than that corresponding to a terminal Se–I, as found in 2,4,6-tri-*tert*-butylphenyl(iodo)selenide [d(Se··I) = 2.529(1) Å].[71] The very pronounced lengthening of the I(1)··Br(1) bond [d(I··Br) = 3.129(1) Å] corresponds to a strong Br(1)–I(2) interaction [d(Br··I) = 2.803(1) Å] with the consequence that **IV** should be better described as an ionic $[2I]^+IBr_2^-$ compound, with the ions strongly interacting with each other. In fact, here, IBr_2^- is not very different from that found in $CsIBr_2$ (bond distances 2.78 and 2.62 Å)[60] and in one of the two asymmetric IBr_2^- groups of $(BPH)^+(H_3O)^+(IBr_2^-)_2$ (2.783(2) and 2.626(3) Å).[68] The sum of the two I-Br bond distances is only 0.048 and 0.039 Å longer than that of $CsIBr_2$ and $(BPH)^+(H_3O)^+(IBr_2^-)_2$ respectively, probably as a consequence of the I(1)··Br(1) interaction. In the crystallographically characterized IBr_2^- ions, the sum of the two I-Br bond distances ranges from 5.36 Å, as found in α-$(PEDTTTF)_2IBr_2$[58] and (BBDT-TTF)IBr_2,[63] to 5.424 Å as in α(BEDT-TTF)$_2IBr_2$[64] and (BBDT-TTF)IBr_2,[63] the mean value calculated over all the reported ions being 5.4 Å.[55-67,76]

The FT-Raman spectrum of **IV** agrees well with the $[2I]^+IBr_2^-$ formulation. All the assignments reported for the IBr_2^- ions are collected in Table 10. Among the reported compounds, only $CsIBr_2$[60] and $(n\text{-}Bu)_4NIBr_2$ [bond distances 2.678(2) and 2.704(2) Å)][55] have also been crystallographically characterized and both ions are asymmetric. All the three expected vibrations of our IBr_2^- ion are infrared and Raman active and were tentatively assigned by analogy with $CsIBr_2$. The broad-strong infrared band at 139 cm^{-1}, assigned to ν_1, probably corresponds to the Raman band at 144 cm^{-1}, but it might also contain contributions of the bands at 153 and 126 cm^{-1}.

In spite of the complexity of the crystal structure of **III**, its FT-Raman spectrum is very simple since only one peak at 170 cm^{-1} dominates over all the others. In fact, taking the intensity of this peak equal to 10, the peak at 214 cm^{-1} and those at 128 (broad) and 111 (broad) cm^{-1} (which can be envisaged in the envelope between 140 and 90 cm^{-1}) have intensities of 0.6, 0.6, and 0.7 respectively. The band at 170 cm^{-1} well agrees with the presence of slightly perturbed diiodine molecules and must consequently be attributed to the diiodine molecules not directly bonded to the selenium atoms. In fact, this frequency falls fairly well within the correlation of ν(I–I) *versus* d(I–I), found for weak or medium–weak CT-complexes of S-donors,[42,44] if the values of the slightly perturbed diiodine molecules are taken as d(I–I).

It is very difficult to ascertain the number and position of all the bands from the broad envelop between 149–90 cm^{-1}; however, the vibrations related to the Se–I–I system should fall in this range. It seems important to point out that the intensity of the ν(I–I) Raman bands arising from the slightly perturbed I_2 is much higher than the Raman bands arising from the Se–I–I system. The FT-Raman spectrum, carried out in solution, can help in identifying the bands related to the Se–I–I group. In fact, the FT-Raman spectrum of a 1:1 mixture of **2** and diiodine ([**2**] = 0.035 M) in CH_2Cl_2 solution shows only two peaks at 139 and 108 cm^{-1}, which must be ascribed to the Se–I–I three-body system.[42,77] It is important to point out that strong adducts, such as those obtained with the selenium compounds, generally show two peaks both in solid state and in solution, whereas weak adducts, such as those obtained with

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(76) Leung, P. C. W.; Emge, T. J.; Schultz, A. J.; Beno, M. A.; Carlson, K. D.; Wang, H. H.; Firestone, M. A.; Williams, J. M. *Solid State Commun.* **1986**, *57*, 93.

Table 9. Far FT-IR[a] and FT-Raman[b] Bands (cm^{-1}) of all the Reported Compounds of *N*-Methyl-1,3-thiazolidine-2(3*H*)-selone (**1**) and *N*-Methylbenzothiazole-2(3*H*)-selone (**2**).

compd	mode of observn	all bands[c] between 300 and 80 cm^{-1}
1·I_2 (**I**)	Raman	278 (0.5), 230 (1.2), 127 (10), 118 (10), 110 sh
	IR	278 m, 251 w, 230 m, 129, vsb, 114 vsb
1·$I_{1.25}Br_{0.75}$ (**II**)	Raman	279 (0.6), 233 (2), 135 (10), 115 (2), 100 sh
	IR	278 m, 253 w, 228 m, 131 vsb, 108 vsb
1·IBr	Raman	279 (0.6), 235 (2), 142 (10), 105 (0.6)
	IR	278 m, 234 m, 145 s, 129 vsb
2·2I_2 (**III**)	Raman	214 (0.6), 170 (10), 128 (0.6, b), 111 (0.7, b)
	IR	260 svb, 206 m, 172 s, 123 s, 96 w
2·IBr	Raman	269 (0.5), 210 (1, b), 158 (10), 131 (8), 110 (4)
	IR	265 m, 235 m, 214 ms, 136 vsb, 123 vs
2·2IBr (**IV**)	Raman	235 (5), 184 (10), 153 (4), 144 (3.5), 126 (1), 101 (0.5), 94 (0.5)
	IR	258 w, 228 m, 185 s, 139 msb, 102 w, 89 ms

[a] Symbols: v = very, s = strong, m = medium, w = weak, b = broad. [b] In the FT-Raman spectra, the values in parentheses represent the intensities of the peaks relating to the strongest, taken equal to 10. [c] See Discussion for the tentative assignments of some bands related to the Se−I−X (X = I, Br) groups.

Table 10. Infrared and Raman Assignments of the IBr_2^- Ion Vibrations (cm^{-1}) for Solid Samples

compd	mode of observn	ν_1	ν_2	ν_3	other bands	ref
$CsIBr_2$[a]	IR	143 m	98 m		192 m	72
	Raman	144 (5)		178 (10)	197 (1), 186 (6), 129 (1, b), 70 (1, b), 40 (1, b)	72
	IR				190 s, 141 s	73
	Raman				188 s, 178 s, 145 m, 131 w, 70, 45	73
$RbIBr_2$	IR	144 m	97 m		195 m	72
	Raman	146 (6)		180 (10)	190 (6), 130 (1, b)	72
$(CH_3)_4NIBr_2$	IR		98 w	171 s	70 w	72
	Raman	160				72
	IR			171 s		73
	Raman	160 vs			138 vw	73
$(n\text{-Bu})_4NIBr_2$[a]	IR				166 sb	55
	Raman				168 s, 138 w	55
	IR		65	169		74
	Raman	168				74
	Raman	163				72
$[\mathbf{2}I]^+IBr_2^-$	IR	139 msb	89 ms	185 s	258 w, 228 m, 102 w, 70 m, 65 m	present work
	Raman	144 (3.5)	94 (0.5)	184 (10)	235 (5), 153 (4), 126 (1), 101 (0.5), 79 (2.5), 71 (2.5), 63 (2.5)	present work

[a] For $CsIBr_2$ and $(n\text{-Bu})_4NIBr_2$ the crystal structures have also been reported.[60,74] In both structures IBr_2^- is asymmetric with 2.78, 2.62 Å and 2.704(2), 2.687(2) Å bond distances, respectively. For the symbols, see note in Table 9.

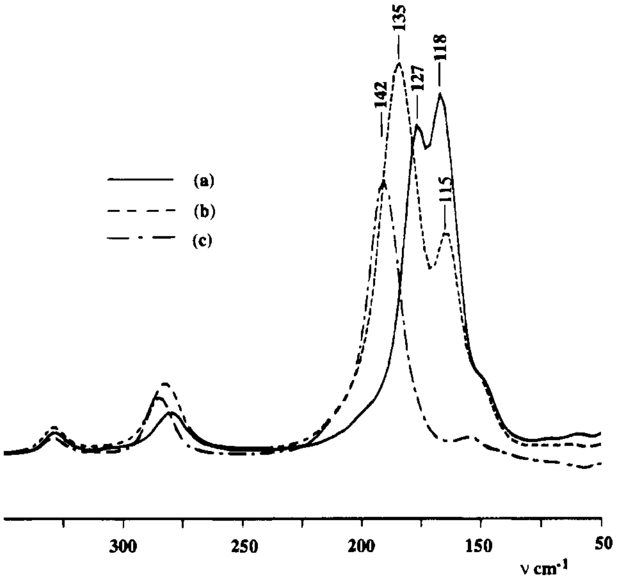

Figure 6. FT-Raman spectra of the solid samples of (a) **1**·I_2 (**I**), (b) **1**·$I_{1.25}Br_{0.75}$ (**II**), and (c) **1**·IBr.

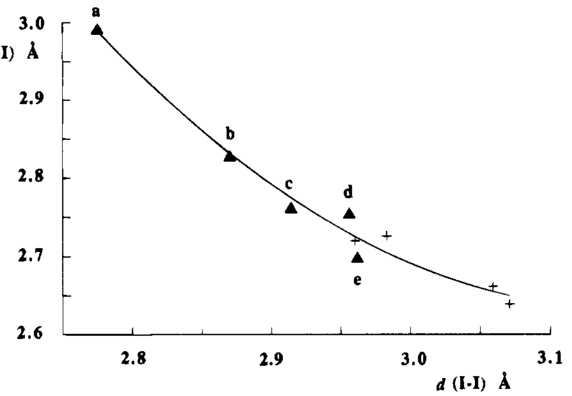

Figure 7. Variation of *d*(Se···I) with *d*(I···I) for the present structures (+) and cyclic dimer of diphenyldiselenane·I_2 (a),[18] 1,4-diselenane·2I_2 (b),[15] tetrahydroselenophene·I_2 (c),[16] 1-oxa-4-selenacyclohexane·I_2 (d)[17] and 5,5-dimethyl-2-selenoxoimidazolidin-4-one·I_2 (e).[54]

the sulfur compounds, show only one peak, whose frequency depends on the strength of the donor−I_2 interaction.[42,77] However, in this particular case, the FT-Raman spectrum, carried out in solution, changes in time with a lowering of these two peaks and the appearance of two new bands at 207 and 121 cm^{-1} (very strong as compared with the others), due to the formation of the previously described[4] solid $[(\mathbf{2})_2I]^+I_3^-$. The latter peak was attributed to the Raman active band of the symmetric I_3^- ion.[4] In fact, the spectrum, recorded on the solution after filtration to separate the solid $[(\mathbf{2})_2I]^+I_3^-$, becomes that of a freshly prepared solution with a lower concentration.

On the contrary, the FT-Raman spectrum of a 1:1 mixture of **2** and IBr ([**2**] = 0.035 M) in CH_2Cl_2 solution does not change in time but shows two broad peaks at 123 and 160 cm^{-1}, at a

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(77) Klaboe, P. *J. Am. Chem. Soc.* **1967**, *89*, 3667.

higher energy with respect to the peaks at 108 and 139 cm^{-1}, found for **2**·I_2, in accordance with an increase in the force constant of Se−I bond[77] and a decrease in the mass on passing from Se−I−I to Se−I−Br. The band at higher energy could be tentatively assigned to the ν_{as}(Se−I−X) with a major contribution of the Se−I vibration and that at lower energy to the ν_s(Se−I−X) with a major contribution of the I−X. The values at 108 and 139 cm^{-1}, found for the Se−I−I system in **2**·I_2, are very close to the values reported in the literature for asymmetric I_3^- ions, and therefore suggest its presence in solution. However, since $[(\mathbf{2})_2I]^+I_3^-$ is very insoluble, we can exclude the presence of I_3^- in solution and attribute the bands to the Se−I−I system.

Analogous observations could be made on the solution spectra of 1:1 mixtures of **1** with I_2 and IBr. However, in this case, for solubility reasons, the bands are very low. The FT-Raman spectrum of a 1:1 mixture of **1** and I_2 ([**1**] = 0.02 M) in CH_2Cl_2 solution shows two very small−broad peaks at 117 and 139 cm^{-1}, which are very close to those found for **2**. In the 1:1 mixture of **1** and IBr ([**1**] = 0.005 M) only one very small peak at 150 cm^{-1} is visible, perhaps as a consequence of the very low concentration of the solution.

A confirmation of these attributions for the Se−I−X three-body system arises from the FT-Raman spectra (Figure 6) of the solid compounds obtained by reacting **1** with I_2 and IBr. **I** (Figure 6a) shows two strong peaks at 118 and 127 cm^{-1}, to which the infrared bands at 114 vsb and 129 vsb cm^{-1} correspond. These can be attributed to the ν_s and ν_{as} vibrations of the Se−I−I three-body system. This is supported by the FT-Raman spectra of **1**·$I_{1.25}Br_{0.75}$ (**II**) and **1**·IBr, reported in Figure 6b,c, respectively. The medium band at 115 cm^{-1}, present in **II**, well agrees with the presence of the crystals of an excess of iodine with respect to bromine and corresponds to the peak of **I** at 118 cm^{-1}. The spectrum of a sample of pure **1**·IBr (Figure 6c) allows to demonstrate that the band at 115 cm^{-1}, present in **II**, is related to the presence of Se−I−I; the absence of this band shifts the peak attributable to ν_{as}(Se−I−Br) from 135 cm^{-1} to 142 cm^{-1}. However, the two bands at 135 and 142 cm^{-1} in Figure 6b,c, respectively would also be attributed to ν_s(Se−I−Br) with a high contribution of ν(I−Br). To support the latter attribution, we report the plot of ν(I−Br) *versus* *d*(I−Br) (Figure 8), obtained by considering the values of solid IBr [d(I−Br) = 2.521(4)],[78] 1,4-dithiacyclohexane·2IBr [2.646(1)][53,79] and 5,5-dimethylimidazoline-2-thione·IBr [2.738(1)],[54] which are all crystallographically characterized. The decrease in the ν(I−Br) stretching frequency follows a linear correlation in analogy with that found for the weak or medium-weak CT-complexes of diiodine.[4,42] Finally, the Raman peaks of *N*-methylbenzothiazole-2-(3*H*)-selone−iodine monobromide (**2**·IBr) at 158(10), 131(8), and 110(4) cm^{-1} can be attributed to the ν_{as}, ν_s, and δ of the Se−I−Br group, respectively. In correspondence with the two Raman peaks at 158(10) and 131(8) cm^{-1}, the infrared spectrum of the latter compound shows only one strong-broad peak at 136 cm^{-1}.

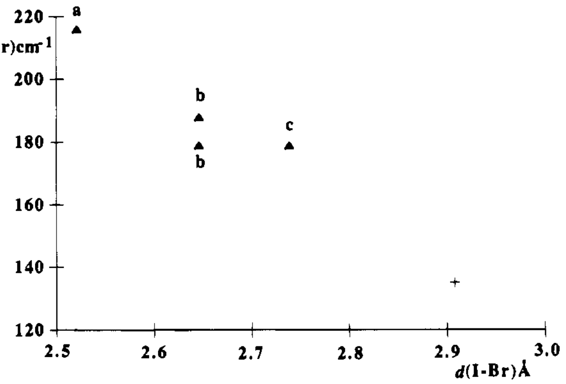

Figure 8. Linear correlation between ν(I−Br) in cm^{-1} FT-Raman bands *vs* *d*(I−Br) in Å for solid IBr (a),[78] 1,4-dithiacyclohexane·2IBr (b),[53,79] 5,5-dimethylimidazolidine-2-thione·IBr (c),[54] and **1**·$I_{1.25}Br_{0.75}$ (**II**) (+).

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters and hydrogen atom locations (26 pages). Ordering information is given on any current masthead page.

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(78) Swink, L. N.; Carpenter, G. B. *Acta Crystallogr.* **1968**, *B24*, 429.

(79) The FT-Raman spectrum of 1,4-dithiacyclohexane·2IBr had not been reported before. In contrast with the fact that only one I−Br bond distance has been reported for the two IBr, the spectrum shows two bands at 188 and 177 cm^{-1} indicating that in the crystals two differently elongated IBr bonds should be present.