Synthesis, Characterization, and Crystal Structures of New Dications Bearing the −Se−Se− Bridge

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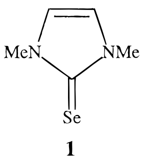
Starting from 1,3-dimethyl-4-imidazoline-2-selone (**1**), 1,2-bis(2-selenoxo-3-methyl-4-imidazolinyl-2-)ethane (**3**) and 1,3-dimethylimidazolidine-2-selone (**4**), the following six compounds, $[(C_5H_8N_2Se-)_2]^{2+}\cdot 2Br^-$ (**I**), $[(C_5H_8N_2Se-)_2]^{2+}\cdot 2I^-$ (**II**), $[(C_5H_8N_2Se-)_2]^{2+}\cdot Cl^-\cdot I_3^-$ (**III**) $[(C_5H_{10}N_2Se-)_2]^{2+}\cdot Br^-\cdot IBr_2^-$ (**IV**), $[(C_5H_7N_2Se-)_2]^{2+}\cdot I_3^-\cdot {}^1/_2I_4^-$ (**V**) and $[(C_5H_7N_2Se-)_2]^{2+}\cdot 2I^-\cdot CH_3CN$ (**VI**), in which the selenium compounds are oxidized to dications bearing the uncommon −Se−Se− bridge, have been prepared, and **I**−**V** crystallographically characterized. **I** and **III** were obtained by reacting **1** with IBr and ICl respectively, while **II** was obtained by reduction of previously described hypervalent selenium compound of **1** (**5**) bearing the I−Se−I group with elemental tellurium. These three compounds contain the same $[(C_5H_8N_2Se-)_2]^{2+}$ dication balanced by two bromides in **I**, two iodides in **II**, and Cl^- and I_3^- in **III**. However, on the basis of the Se−Cl bond length of 2.778(5) Å, **III** can also be considered as formed by the $[(C_5H_8N_2Se-)_2Cl]^+$ cation, with I_3^- as counterion. Similarly to **III**, compound **IV**, which was obtained by reacting **4** with IBr, can be considered as formed by $[(C_5H_{10}N_2Se-)_2Br]^+$ cations and IBr_2^- anions. As in **II**, compound **V** has been prepared by reduction of the hypervalent selenium compound of **3** (**6**) bearing two I−Se−I groups with elemental tellurium. In **V**, the $[(C_5H_7N_2Se-)_2]^{2+}$ cation is balanced by I_3^- and half I_4^{2-} anions. The structural data show that all the cations are very similar, with Se−Se bond lengths ranging from 2.409(2) to 2.440(2) Å. FT-IR and FT-Raman spectra of **I**−**VI** allow one to identify two bands around 230 ± 10 and 193 ± 5 cm^{-1} that are common to all compounds. These bands are generally strong in the FT-Raman and weak in the FT-IR spectra and should contain a contribution of the ν(Se−Se) stretching vibration. The spectra are also in good agreement with the structural features of the polyhalide anions present in the crystals. Crystallographic data are as follows: **I** is monoclinic, space group $P2_1$, with $a = 9.849(6)$ Å, $b = 11.298(5)$ Å, $c = 7.862(6)$ Å, $\beta = 106.44(2)°$, $Z = 2$, and $R = 0.0362$; **II** is monoclinic, space group $P2_1$, with $a = 8.063(6)$ Å, $b = 11.535(5)$ Å, $c = 10.280(5)$ Å, $\beta = 107.13(2)°$, $Z = 2$, and $R = 0.0429$, **III** is monoclinic, space group $P2_1/n$, with $a = 10.431(7)$ Å, $b = 18.073(5)$ Å, $c = 11.223(6)$ Å, $\beta = 100.76(2)°$, $Z = 4$, and $R = 0.0490$; **IV** is monoclinic, space group $P2_1/n$, with $a = 10.298(5)$ Å, $b = 18.428(7)$ Å, $c = 11.475(6)$ Å, $\beta = 104.10(4)°$, $Z = 4$, and $R = 0.0300$; **V** is triclinic, space group $P\bar{1}$, with $a = 7.456(6)$ Å, $b = 11.988(5)$ Å, $c = 12.508(5)$ Å, $\alpha = 79.32(2)°$, $\beta = 85.49(2)°$, $\gamma = 80.62(2)°$, $Z = 2$, and $R = 0.0340$.

Introduction

As a further contribution to the studies concerning the donor/acceptor interaction between sulfur and selenium containing compounds and diiodine, we have recently[2] reported the characterization of three products obtained by reacting 1,3-dimethyl-4-imidazoline-2-selone (**1**), 1,1′-bis(2-selenoxo-3-methyl-4-imidazolinyl)methane (**2**) and 1,2-bis(2-selenoxo-3-methyl-4-imidazolinyl)ethane (**3**) with I_2.



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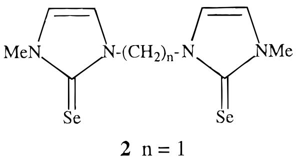
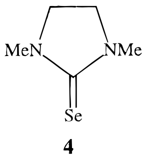


2 n = 1
3 n = 2



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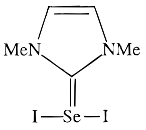

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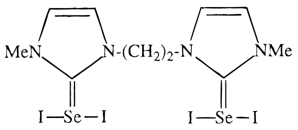

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In spite of similar electronic, infrared, and Raman spectra of the obtained products, their crystal structures showed that only **2** yielded the expected donor−acceptor complex bearing the Se−I−I arrangement;[3] **1** and **3** gave rise to the stable hypervalent 10-Se-3 compounds **5** and **6**,[4] characterized by the linear I−Se−I moiety. These and many other results reported in the literature[5−22] show the minor changes in the structure of the donor molecules or in that experimental conditions (solvent, reaction molar ratios, ...) can lead to unpredictable products. For this reason, X-ray structural characterization has often been

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(1) (a) Università di Parma and CNR. (b) Università di Milano. (c) Università di Cagliari.

(2) Bigoli, F.; Pellinghelli, A. M.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Mercuri, M. L.; Trogu, E. F. *Gazz. Chim. Ital.* **1994**, *124*, 445. For simplicity, compound **6** is shown in the scheme without the two molecules of dichloromethane present in the structure.

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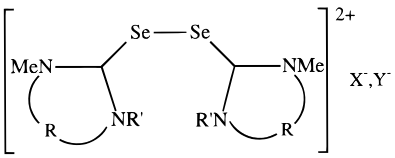
of crucial importance in elucidating their structures. In absence of X-ray data, Raman spectroscopy has been widely employed to hypothesize the nature of the halides, mostly in the field of molecular organic conductors doped with diiodine or interhalogens. The identification of the type of the halide is important because it allows an estimation of the extent of the charge transferred from the donor to the halogen.[23] With the intention of verifying the ability of Raman spectroscopy to provide useful structural information when X-ray determination is not applicable, we started a program of synthesis and characterization of a great number of compounds obtainable by reacting different substrates having sulfur or selenium donor atoms with diiodine and also with other halogens and interhalogens (Br_2, IBr, ICl).

With the latter acceptors of increasing strength, the variability in the structure of the solid compounds obtainable can be increased further, as shown by the results reported in this paper. We report here the X-ray and Raman characterization of six compounds containing new dications having the uncommon −Se−Se− bridge; three of them have been obtained by reacting **1** and **4** with IBr or ICl while the remaining was obtained by means of a new synthetic route consisting of the reduction of **5** and **6** with metallic tellurium.

Experimental Section

Materials. Starting materials, 1,3-dimethyl-4-imidazoline-2-selone (**1**), 1,2-bis(2-selenoxo-3-methyl-4-imidazolinyl)ethane (**3**), 1,3-dimethylimidazolidine-2-selone (**4**), 1,3-dimethyl-4-imidazolin-2-ylium diiodoselenanide (**5**) and ethylene-1,2-bis(3-methyl-4-imidazolin-2-ylium diiodoselenanide)−bis(dichloromethane) (**6**) were prepared according to the literature.[2,24]

Chart 1



	R	R'	X	Y
I	CH=CH	Me	Br	Br
II	CH=CH	Me	I	I
III	CH=CH	Me	Cl	I_3
IV	CH_2-CH_2	Me	Br	IBr_2
V	CH=CH	CH_2-	I_3	$1/2I_4$
VI	CH=CH	CH_2-	I	I

Compounds $[(C_5H_8N_2Se-)_2]^{2+}\cdot 2Br^-$ (I), $[(C_5H_8N_2Se-)_2]^{2+}\cdot Cl^-\cdot I_3^-$ (III), and $[(C_5H_{10}N_2Se-)_2]^{2+}\cdot Br^-\cdot IBr_2^-$ (IV). Compounds **I**, **III**, and **IV** were prepared from mixtures (1/1 molar ratio) of **1** and IBr, **1** and ICl, and **4** and IBr in CH_2Cl_2, CH_2Cl_2/petroleum ether (2/1 v/v), and CCl_4 solutions respectively (see Chart 1).

I (yellow crystals): Anal. Found (calcd for $C_{10}H_{16}Br_2N_4Se_2$): C, 23.55 (23.32); H, 3.16 (3.16); N, 10.99 (11.78).

III (black crystals): Anal. Found (calcd for $C_{10}H_{16}ClI_3N_4Se_2$): C, 15.95 (15.65); H, 2.20 (2.10); N, 7.60 (7.30).

IV (black crystals): Anal. Found (calcd for $C_{10}H_{20}Br_3IN_4Se_2$): C, 16.74 (16.64); H, 3.04 (2.77); N, 8.10 (7.77).

Compound $[(C_5H_8N_2Se-)_2]^{2+}\cdot 2I^-$ (II). A mixture of **5** (500 mg, 1.16 mmol), tellurium powder (300 mg, 2.33 mmol), and Et_2O (50 mL, freshly distilled over $LiAlH_4$ and degassed) was stirred at room temperature and under N_2 atmosphere for 7 days. The residue obtained by filtration was washed with Et_2O, dried under vacuum, and treated with hot CH_3CN. The hot suspension was filtered and orange crystals of **II** were obtained from the filtrate. Anal. Found (calcd for $C_{10}H_{16}I_2N_4Se_2$): C, 20.22 (19.86), H, 2.73 (2.64); N, 9.35 (9.37).

Compounds $[(C_5H_7N_2Se-)_2]^{2+}\cdot I_3^-\cdot {}^1/_2 I_4^-$ (V) and $[(C_5H_7N_2Se-)_2]^{2+}\cdot 2I^-\cdot CH_3CN$ (VI). A mixture of **6** (449 mg, 0.47 mmol), tellurium powder (120 mg, 0.94 mmol), and Et_2O (50 mL, freshly distilled over $LiAlH_4$ and degased) was stirred at room temperature and under N_2 atmosphere for 2 weeks. The residue obtained by filtration was washed with Et_2O, dried under vacuum, and treated with hot CH_3CN (50 mL). The hot suspension was filtered and the filtrate allowed to stand one night at −20 °C. Yellow microcrystals of **VI**, containing one molecule of solvent, were formed and recollected by filtration. Black crystals of **V** were obtained from the mother liquor by slow evaporation.

V (black crystals): Anal. Found (calcd for $C_{10}H_{14}I_5N_4Se_2$): C, 12.64 (12.20); H, 1.49 (1.42); N, 5.81 (5.69).

VI (yellow crystals): Anal. Found (calcd for $C_{12}H_{17}I_2N_5Se_2$): C, 23.10 (22.70); H, 2.66 (2.64); N, 11.16 (10.88).

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. All spectra were recorded at 4 cm^{-1} resolution, down to about 80 cm^{-1} Raman shift. 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 Determinations. A summary of the crystallographic data is given in Table 1. The diffraction measurements were made on Enraf Nonius CAD4 (for **I** and **IV**), Siemens AED (for **II**), and Philips PW 1100 (for **III** and **V**) diffractometers with Mo Kα radiation (graphite crystal monochromator). The data were collected using the $\theta-2\theta$ method for **I**−**III** and **V**, and the ω-scan method for **IV**. Intensity data (1474, 2321, 1676, 1771, and 3556 observed reflections for **I**−**V**, respectively) were corrected for Lorentz and polarization factors and for absorption by following the empirical method of North *et al.*[25] for **IV** and that of Walker and

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(3) In CH_2Cl_2 solution, with I_2 compound **4** gives the usual 1:1 charge-transfer complex with formation constant $K = (4.95 \pm 0.22) \times 10^5$ $dm^3\cdot mol^{-1}$; Devillanova, F. A.; Verani, G. *Tetrahedron* **1981**, *37*, 1803. The crystal structure of the solid product has not been solved since it has not been possible to obtain suitable crystals so far.

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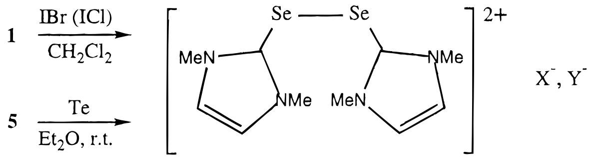
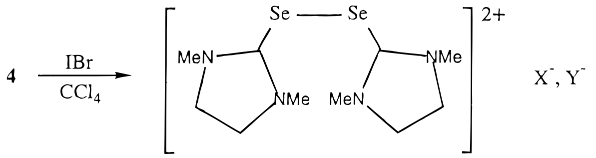
Stuart[26] for the others. The structures were solved by Patterson and Fourier methods and the final full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms for **I**, **II**, **IV**, and **V** and for Se, I, and Cl atoms only for **III**, the weighting scheme being $w = k/[\sigma^2(F_o)+gF_o^2]$. All hydrogen atoms were placed at their geometrically calculated positions. As the space group $P2_1$ is free of reflective elements, it was necessary to determine the absolute configuration of the crystal for **I** and **II**. Final refinement of the corrected configuration resulted in $R = 0.0362$ and $R_w = 0.0405$, $R = 0.0429$ and $R_w = 0.0662$ for **I** and **II** respectively. The corresponding values obtained by refinement of the inverted structure are $R = 0.0386$ and $R_w = 0.0459$, $R = 0.0466$ and $R_w = 0.0686$. Scattering factors and corrections for anomalous dispersion effects were from ref 27. Calculations for compounds **I**–**III** and **V** were carried out on Gould Powernode 6040 and Encore 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica del CNR" (Parma). The system of computer programs SHELX-76[28] and SHELXS-86[29] and the programs ABSORB,[30] PARST,[31] PLUTO,[32] and ORTEP[33] were used. For compound **IV**, all the calculations were performed at the "Dipartimento di Chimica Strutturale e Stereochimica Inorganica (Milano)" on an HP Vectra 486/33 computer using the Personal Structure Determination Package.[34]

Results

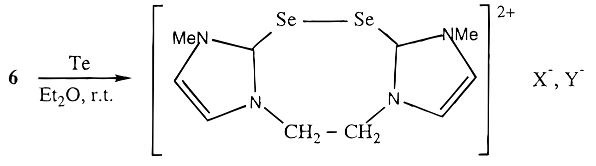
The synthetic routes to achieve the products under discussion are summarized as follows:



I (X = Y = Br)
II (X = Y = I)
III (X = Cl, Y = I$_3$)



IV (X = Br, Y = IBr$_2$)



V (X = I$_3$, Y = 1/2I$_4$)
VI (X = Y = I)

Table 1. Crystallographic Data

	I	II	III	IV	V
formula	$C_{10}H_{16}Br_2$-N_4Se_2	$C_{10}H_{16}I_2$-N_4Se_2	$C_{10}H_{16}ClI_3$-N_4Se_2	$C_{10}H_{20}Br_3$-IN_4Se_2	$C_{10}H_{14}I_5$-N_4Se_2
fw	509.99	603.99	766.35	720.85	982.69
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.849(6)	8.063(6)	10.431(7)	10.298(5)	7.456(6)
b, Å	11.298(5)	11.535(5)	18.073(5)	18.428(7)	11.988(5)
c, Å	7.862(6)	10.280(5)	11.223(6)	11.475(6)	12.508(5)
α, deg					79.32(2)
β, deg	106.44(2)	107.13(2)	100.76(2)	104.10(4)	85.49(2)
γ, deg					80.62(2)
V, Å^3	839.1(9)	913.7(9)	2079(2)	2112(2)	1083(1)
Z	2	2	4	4	2
d_{calcd}, g/cm^3	2.019	2.195	2.449	2.267	3.015
λ(Mo kα), Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
temp, K	295	295	295	295	295
μ, cm^{-1}	91.59	74.17	81.39	105.3	105.44
R^a	0.0362	0.0429	0.0490	0.0300	0.0340
$R_w{}^b$	0.0405	0.0662	0.0618	0.0360	0.0458

^{a} $R = \sum|\Delta F|/\sum|F_o|$. ^{b} $R_w = (\sum w(\Delta F)^2/\sum w|F_o|^2)^{1/2}$.

Crystal Structures of $[(C_5H_8N_2Se-)_2]^{2+}\cdot 2Br^-$ (I), and $[(C_5H_8N_2Se-)_2]^{2+}\cdot 2I^-$ (II). The geometrical parameters of **I** and **II** are listed in Table 2 and the final atomic coordinates in Tables 3 and 4 respectively. These compounds consist of a discrete $[(C_5H_8N_2Se-)_2]^{2+}$ dication with a –Se–Se– bridge, balanced by two bromides in **I** and two iodides in **II**. In both structures, the two halides, which interact with the Se atoms in a slightly asymmetric manner [Se(11)···Br(1) = 3.242(2) Å and Se(12)···Br(2) = 3.165(2) Å in **I** and Se(11)···I(1) = 3.410(2) Å and Se(12)···I(2) = 3.330(2) Å in **II**], lie roughly perpendicular to the corresponding imidazoline ring, with X–Se–C–N torsion angles of 81.1(9) and 82.4(10)° for X = Br and 82.6(8) and 82.9(9)° for X = I; the X–Se–Se–X fragment is almost linear [X–Se–Se angles: 164.16(4) and 177.04(6)° in **I** and 165.78(5) and 176.00(6)° in **II**]. In both structures, the cation and the anion, which are involved in the shortest contact, act as bridges through a secondary contact [Se(11)···Br(2) $(1 - x, y - {}^1/_2, -z)$, 3.506(2) Å, and Se(11)···I(2) $(-x, {}^1/_2 + y, 2 - z)$, 3.627(2) Å], thus determining tetracoordination for Se(11) and the formation of chains parallel to *b*.

Crystal Structure of $[(C_5H_8N_2Se-)_2]^{2+}\cdot Cl^-\cdot I_3^-$ (III) and $[(C_5H_{10}N_2Se-)_2]^{2+}\cdot Br^-\cdot IBr_2^-$ (IV). The structures of **III** and **IV**, in analogy with those of **I** and **II**, can be described as discrete $[(C_5H_8N_2Se-)_2]^{2+}$ (for **III**) and $[(C_5H_{10}N_2Se-)_2]^{2+}$ (for **IV**) dications balanced by Cl^- and I_3^- in **III** and Br^- and IBr_2^- in **IV** (see Tables 2, 5, and 6). However, on the basis of the Se–Cl and Se–Br bond lengths of 2.778(5) and 2.830(1) Å respectively, they can also be considered as formed by the $[(C_5H_8N_2Se-)_2Cl]^+$ and $[(C_5H_{10}N_2Se-)_2Br]^+$ (Figure 1) cations, having I_3^- and IBr_2^- as counterions respectively. In both structures, two cations and two anions, related by a symmetry center, are alternatively coupled in such a way that an eight-membered ring with a chair conformation is formed (Figure 2 for **III**).

In **IV**, the presence of anomalous thermal parameters of the bromine atoms of the IBr_2^- ion in the early stages of the refinement and a persisting high value of the final *R* index suggested that some I_3^- or I_2Br^- anions could be cocrystallized during the crystal growth with partial replacement of the IBr_2^- anions. A refinement of the multiplicity of the Br(1) and Br-

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Table 2. Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for Compounds $(C_5H_8N_2Se-)_2Br_2$ (**I**), $(C_5H_8N_2Se-)_2I_2$ (**II**), $[(C_5H_8N_2Se-)_2Cl]I_3$ (**III**), $[(C_5H_{10}N_2Se-)_2Br]IBr_2$ (**IV**), and $(C_5H_7N_2Se-)_2I_3\cdot{}^1/_2I_4$ (**V**)[a]

	I	II	III	IV	V
Se(11)−Se(12)	2.409(2)	2.434(2)	2.440(2)	2.424(1)	2.416(2)
Se(11)−C(11)	1.87(1)	1.88(1)	1.90(1)	1.90(1)	1.900(5)
Se(12)−C(12)	1.87(1)	1.88(1)	1.91(1)	1.90(1)	1.887(6)
N(11)−C(11)	1.37(1)	1.33(1)	1.27(2)	1.31(1)	1.362(8)
N(11)−C(31)	1.39(2)	1.37(1)	1.40(2)	1.47(1)	1.389(8)
N(11)−C(41)	1.45(1)	1.48(1)	1.48(2)	1.45(1)	1.462(8)
N(21)−C(11)	1.33(1)	1.34(1)	1.38(2)	1.29(1)	1.326(7)
N(21)−C(21)	1.38(1)	1.36(2)	1.36(2)	1.47(1)	1.385(8)
N(21)−C(51)	1.49(1)	1.47(2)	1.46(2)	1.43(1)	1.455(9)
N(12)−C(12)	1.34(2)	1.34(1)	1.32(2)	1.30(1)	1.349(8)
N(12)−C(32)	1.37(2)	1.36(2)	1.38(2)	1.46(1)	1.372(8)
N(12)−C(42)	1.48(1)	1.46(1)	1.46(2)	1.43(1)	1.474(8)
N(22)−C(12)	1.36(1)	1.33(1)	1.33(2)	1.30(1)	1.345(7)
N(22)−C(22)	1.39(1)	1.34(2)	1.38(2)	1.47(1)	1.375(9)
N(22)−C(52)	1.47(2)	1.49(2)	1.47(2)	1.44(1)	1.467(8)
C(21)−C(31)	1.34(2)	1.37(2)	1.35(2)	1.52(1)	1.335(10)
C(22)−C(32)	1.36(2)	1.38(2)	1.35(2)	1.49(1)	1.347(9)
Se(11)−Cl			2.778(5)		
I(1)−I(2)			2.855(3)		2.937(1)
I(2)−I(3)			2.917(3)		2.914(1)
I(4)···I(5)					3.405(2)
I(5)−I(5^i)					2.819(1)
Se(11)−Br				2.830(1)	
I(1)−Br(1)				2.744(1)	
I(1)−Br(2)				2.815(1)	
Se(12)−Se(11)−C(11)	95.7(3)	96.0(3)	94.0(4)	91.7(2)	96.1(2)
Se(11)−Se(12)−C(12)	98.1(3)	98.3(3)	97.8(4)	97.9(2)	98.9(2)
C(31)−N(11)−C(41)	125.6(9)	124.3(10)	121.4(12)	120.1(8)	125.2(5)
C(11)−N(11)−C(41)	125.0(9)	125.1(9)	125.6(12)	128.0(7)	126.9(5)
C(11)−N(11)−C(31)	108.4(9)	110.8(9)	112.8(12)	109.6(7)	107.8(5)
C(21)−N(21)−C(51)	124.4(9)	122.9(10)	127.7(13)	121.5(8)	124.2(5)
C(11)−N(21)−C(51)	124.9(8)	126.1(9)	125.5(13)	127.5(8)	127.2(5)
C(11)−N(21)−C(21)	110.7(9)	110.9(9)	106.8(13)	110.9(7)	108.6(5)
C(32)−N(12)−C(42)	124.7(10)	123.0(10)	122.6(14)	121.3(8)	124.9(5)
C(12)−N(12)−C(42)	124.9(10)	127.7(9)	128.4(13)	129.1(8)	125.7(5)
C(12)−N(12)−C(32)	110.3(10)	109.3(9)	109.0(13)	109.5(8)	109.4(5)
C(22)−N(22)−C(52)	124.7(11)	124.5(14)	123.4(12)	121.9(7)	124.9(5)
C(12)−N(22)−C(52)	126.3(10)	125.7(11)	126.3(13)	128.5(7)	125.5(5)
C(12)−N(22)−C(22)	109.0(9)	109.8(10)	110.3(13)	109.7(7)	109.6(5)
N(11)−C(11)−N(21)	106.4(8)	106.0(8)	107.2(12)	112.7(7)	108.2(5)
Se(11)−C(11)−N(21)	126.4(7)	127.7(7)	124.6(10)	123.7(6)	126.8(4)
Se(11)−C(11)−N(11)	126.9(7)	126.2(7)	128.2(10)	123.6(6)	124.9(4)
N(21)−C(21)−C(31)	106.5(10)	106.4(11)	110.4(15)	101.3(7)	108.1(6)
N(11)−C(31)−C(21)	107.9(11)	105.7(9)	102.8(15)	102.0(7)	107.3(6)
N(12)−C(12)−N(22)	106.7(9)	107.5(9)	107.4(13)	113.6(8)	106.6(5)
Se(12)−C(12)−N(22)	126.2(7)	127.5(7)	126.4(11)	123.4(6)	126.8(4)
Se(12)−C(12)−N(12)	127.0(9)	124.8(8)	126.2(10)	123.0(7)	126.5(4)
N(22)−C(22)−C(32)	106.6(11)	107.6(12)	105.3(13)	102.9(7)	107.0(6)
N(12)−C(32)−C(22)	107.4(11)	105.6(11)	107.9(15)	104.0(7)	107.4(6)
Cl−Se(11)−Se(12)			172.11(12)		
Cl−Se(11)−C(11)			79.4(4)		
I(1)−I(2)−I(3)			175.1(1)		178.47(3)
I(4)···I(5)−I(5^i)					178.82(11)
Br−Se(11)−Se(12)				166.70(4)	
Br−Se(11)−C(11)				77.7(2)	
Br(1)−I(1)−Br(2)				175.69(3)	

[a] Key to symmetry operation (i): 2 − *x*, −*y*, 2 − *z*.

(2) atoms revealed that the Br(1) site, with multiplicity 1.17, corresponds to a composition of 67% bromine and 33% iodine, whereas the Br(2) site, with multiplicity 1.24, corresponds to 53% bromine and 47% iodine. A refinement carried out on a different set of data obtained from another crystal of the same preparation showed a similar disorder with different composition of the Br(1) and Br(2) sites. In both cases the Br and I(1) positions are not at all involved in such a substitutional disorder.

Crystal Structure of $[(C_5H_7N_2Se-)_2]^{2+}\cdot I_3^-\cdot{}^1/_2I_4^-$ (V). **V** consists of a discrete $[(C_5H_7N_2Se-)_2]^{2+}$ dication, in which the Se−Se intramolecular bond brings out an eight-membered ring with a chair conformation (Tables 2 and 7 and Figure 3). The dication is balanced by an I_3^- anion, slightly asymmetric [2.937(1)−2.914(1) Å] and almost linear [178.47(3)°], and half an I_4^{2-} anion. The latter is almost linear and can be considered as formed by the interactions [3.405(2) Å] between two iodides [I(4) and I(4^i)] and a diiodine molecule [I(5)−I(5^i)] which lies on a center of symmetry [(I(4)···I(5)−I(5^i)···I(4^i)]. An I_{10}^{4-} anion with a roughly Z-shaped arrangement is formed when the contacts I(4)···I(1) (1 − *x*, 1 − *y*, 1 − *z*) 4.067(2) Å involving an I_4^{2-} and two I_3^- anions, related by the center of symmetry, are considered (Figure 3).

FT-IR and FT-Raman Spectra. The FT-IR and FT-Raman bands of **I**−**VI**, in the range 300-80 cm^{-1}, are collected in Table

Table 3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for $(C_5H_8N_2Se-)_2$ Br_2 (**I**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Br(1)	87(1)	−21(2)	3434(2)	574(4)
Br(2)	5839(1)	3078(1)	−2019(2)	487(4)
Se(11)	2622(1)	887(0)	1879(1)	418(3)
Se(12)	3969(1)	1807(1)	116(1)	436(3)
N(11)	1319(8)	2878(7)	3060(10)	415(29)
N(21)	232(9)	2435(8)	345(11)	442(32)
N(12)	4323(10)	4155(9)	1610(12)	471(32)
N(22)	5982(9)	2973(8)	3043(11)	445(30)
C(11)	1367(10)	2153(9)	1743(12)	360(35)
C(21)	−502(12)	3357(11)	858(17)	569(49)
C(31)	181(12)	3642(11)	2532(16)	549(43)
C(41)	2353(14)	2876(14)	4862(15)	777(58)
C(51)	−153(12)	1867(12)	−1376(14)	567(43)
C(12)	4770(11)	3035(10)	1680(13)	430(35)
C(22)	6284(14)	4086(12)	3801(16)	621(51)
C(32)	5244(15)	4819(12)	2881(16)	631(53)
C(42)	3070(13)	4630(11)	268(18)	634(49)
C(52)	6881(14)	1920(14)	3586(20)	815(58)

Table 4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for $(C_5H_8N_2Se-)_2I_2$ (**II**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
I(1)	3542.3(10)	5000	5099.7(8)	531(3)
I(2)	−1999.6(9)	1987.4(10)	10883.5(7)	468(2)
Se(11)	1853(1)	4130(1)	7616(1)	378(3)
Se(12)	123(1)	3270(1)	8947(1)	400(3)
N(11)	2901(10)	2116(8)	6418(9)	392(25)
N(21)	300(10)	2589(7)	5363(8)	360(24)
N(12)	1518(13)	968(8)	9320(9)	413(28)
N(22)	2952(10)	2111(12)	10912(9)	474(31)
C(11)	1660(11)	2874(8)	6417(9)	308(26)
C(21)	684(17)	1677(11)	4670(12)	512(44)
C(31)	2369(14)	1376(11)	5329(13)	482(35)
C(41)	4666(15)	2118(13)	7388(14)	613(44)
C(51)	−1373(15)	3197(14)	4930(15)	589(44)
C(12)	1648(12)	2066(9)	9763(9)	360(26)
C(22)	3657(15)	1058(12)	11209(14)	515(40)
C(32)	2778(16)	316(11)	10186(14)	530(41)
C(42)	227(17)	482(11)	8134(13)	510(37)
C(52)	3499(22)	3154(18)	11786(17)	820(61)

8 together with their tentative assignments. As clearly pointed out by the superimposed FT-Raman spectra of **V** and **VI** (Figure 4) and by Table 8, all the Raman spectra show two peaks at 230 ± 10 cm^{-1} and 193 ± 5 cm^{-1}, which have the highest intensities in the absence of polyhalide anions.

Discussion

The dications described in this paper contain the uncommon −Se−Se− bridge whose lengths [ranging from 2.409(2) to 2.440(2) Å; bond order[35] ranging from 0.83 to 0.75] are greater than the covalent radius sum and also than the value of 2.380(4) Å (bond order 0.91) reported for $[(SeC(NH_2)_2]_2Cl_2$.[36] Similar Se−Se bond distances were observed for other types of cations containing a tricoordinated selenium,[37,38] such as Se_{10}^{2+}, in which the Se−Se bond distances fall in the 2.413(9)−2.456(9) Å range.[37] All Se−Se bond distances are longer than the values reported for acyclic neutral diselenides[14,39,40] and those found in the positively charged tetraselenotetracene stacks (both as chloride and thiocyanate derivatives),[39] while they are shorter than the distances reported for the tris(selenourea) cation $[(SeC(NH_2)_2]_3^{2+}$, whose values range between 2.597(2) and 2.717(2) Å for the three reported structures.[39] The values of the selenium−carbon distances correspond to that of a normal single covalent Se−C(sp^2) bond. C(11) is synclinal with respect to the analogous C(12) with similar C−Se−Se−C torsion angle values in all cations. The dihedral angles between the two planar pentaatomic rings range from 28.6(6) to 32.0(4)°. All the halides, interacting with the Se atoms, lie roughly perpendicular to the corresponding pentaatomic ring: the

Table 5. Fractional Atomic Coordinates (× 10^4) and Isotropic Thermal Parameters (Å^2 × 10^4), with Esd's in Parentheses, for $[(C_5H_8N_2Se-)_2Cl]I_3$ (**III**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*
I(1)	7194.7(14)	6520.6(8)	1829.5(14)	837(6)[a]
I(2)	4432.2(12)	6595.4(5)	1045.5(10)	559(5)[a]
I(3)	1642.5(15)	6626.2(8)	45.0(15)	924(6)[a]
Se(11)	2784.3(14)	5273.5(8)	2867.6(14)	385(5)[a]
Se(12)	2541.0(16)	4580.0(9)	973.3(14)	456(6)[a]
Cl	2735(4)	5978(2)	5059(4)	522(15)[a]
N(11)	2442(11)	4045(6)	4388(10)	363(29)
N(21)	597(12)	4464(6)	3515(11)	413(30)
N(12)	3349(13)	3086(7)	1676(11)	480(34)
N(22)	4978(12)	3824(6)	1901(11)	450(32)
C(11)	1931(14)	4543(7)	3660(12)	324(33)
C(21)	377(18)	3886(9)	4220(16)	613(49)
C(31)	1515(17)	3605(9)	4811(16)	553(45)
C(41)	3862(15)	3937(9)	4828(15)	561(47)
C(51)	−366(18)	4927(10)	2755(17)	744(56)
C(12)	3690(14)	3782(7)	1551(13)	358(35)
C(22)	5481(17)	3141(8)	2288(14)	483(41)
C(32)	4450(17)	2675(9)	2099(15)	589(47)
C(42)	2040(18)	2761(10)	1427(17)	761(57)
C(52)	5788(15)	4490(8)	1878(14)	482(41)

[a] Equivalent isotropic *U* defined as one-third the trace of the diagonalized matrix.

Table 6. Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for $[(C_5H_{10}N_2Se-)_2Br]IBr$ (**IV**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
I(1)	4480.2(6)	6614.7(3)	1166.7(5)	629(3)
Br	2595(1)	5914.9(5)	4843.8(8)	720(6)
Br(1)	7215.7(9)	6514.9(5)	1916.2(8)	789(6)
Br(2)	1695(1)	6710.1(6)	219.0(9)	983(7)
Se(11)	2906.6(8)	5224.5(4)	2726.2(7)	499(5)
Se(12)	2641.5(9)	4547.6(5)	871.5(8)	601(6)
N(11)	2347(7)	4053(4)	4138(6)	570(40)
N(12)	3404(7)	3108(4)	1560(6)	613(40)
N(21)	560(6)	4506(4)	2970(6)	590(40)
N(22)	5111(7)	3841(4)	1834(6)	540(40)
C(11)	1847(7)	4545(4)	3330(7)	450(40)
C(12)	3816(8)	3770(4)	1484(6)	477(45)
C(21)	39(9)	3890(5)	3536(9)	870(65)
C(22)	5720(10)	3136(5)	2249(8)	693(60)
C(31)	1260(10)	3692(5)	4538(8)	790(60)
C(32)	4560(10)	2631(5)	1975(8)	803(65)
C(41)	3720(10)	3983(6)	4838(9)	767(70)
C(42)	2070(10)	2829(6)	1250(10)	953(75)
C(51)	−309(9)	4958(6)	2100(10)	967(80)
C(52)	5904(9)	4481(5)	1828(8)	650(60)

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(35) Selenium−selenium bond order, $n = 10^{(2.35-d)/0.71}$, where *d* is the Se−Se bond distance (Å). Pauling, L. *The Nature of the Chemical Bond*, 3rd ed; Cornell University Press: New York, 1960.

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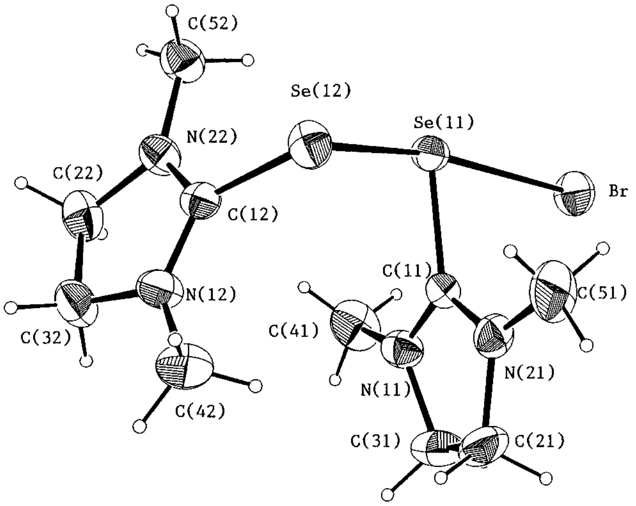

Figure 1. Perspective view of the $[(C_5H_{10}N_2Se-)_2Br]^+$ cation (30% probability ellipsoids).

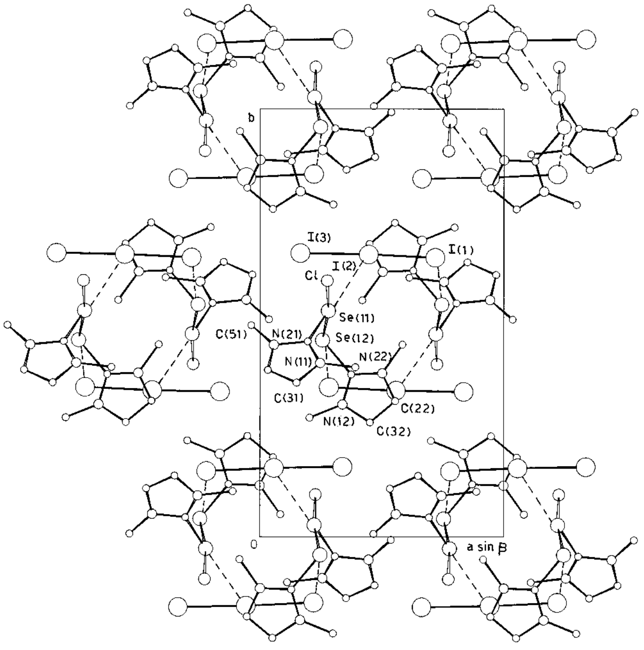

Figure 2. Projection of the structure of **III** along [001].

X−Se−C−N (X = Cl, Br, I) torsion angles are in the range 81.1(9)−109.5(12)°. In all compounds, a non planar tetracoordination for Se(11) and a slightly deformed T-shaped arrangement for Se(12) are observed. In **V**, both Se(11) and Se(12) present tetracoordination. As described in the Results, in **III** (or **IV**), two cations are alternatively coupled with two I_3^- (or IBr_2^-), to create an eight-membered ring with a chair conformation. A similar ring has been described in the centrosymmetric dimer of the charge-transfer adduct between diphenyldiselenane and diiodine.[14] The strong Se···I (Br) interaction in the eight-membered ring probably contributes to the asymmetry of both I_3^- and IBr_2^- in **III** and **IV** respectively.

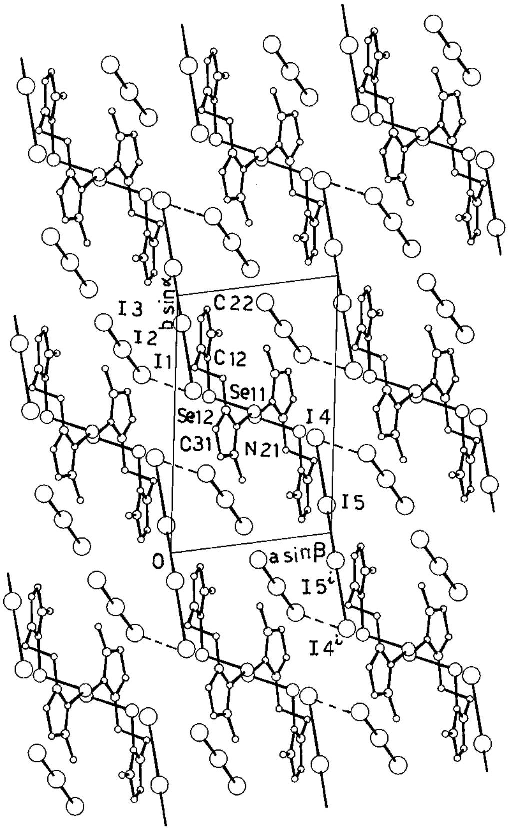

Figure 3. Projection of the structure of **V** along [001].

Table 7. Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4) (One-Third the Trace of the Diagonalized Matrix), with Esd's in Parentheses, for $[(C_5H_7N_2Se-)_2]I_3\cdot{}^1/_2I_4$ (**V**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
I(1)	−2077.8(7)	7076.5(5)	4755.1(4)	517(2)
I(2)	−3309.2(6)	8175.8(4)	6650.8(4)	409(2)
I(3)	−4513.9(9)	9325.1(4)	8497.3(4)	587(2)
I(4)	8872.2(6)	3786.9(4)	7840.0(4)	440(2)
I(5)	9678.0(7)	1101.9(5)	9353.8(4)	524(2)
Se(11)	4966.5(9)	5107.6(5)	6759.2(5)	317(2)
Se(12)	2135.4(9)	5902.1(5)	5901.4(5)	329(2)
N(11)	3195(7)	5292(4)	8884(4)	316(16)
N(21)	3783(7)	3521(4)	8618(4)	306(16)
N(12)	1550(7)	7819(4)	7066(4)	312(16)
N(22)	2161(7)	8359(4)	5349(4)	314(16)
C(11)	3899(8)	4598(5)	8158(4)	279(18)
C(21)	2956(9)	3518(6)	9649(5)	377(21)
C(31)	2586(10)	4603(6)	9815(5)	421(23)
C(41)	2968(9)	6547(5)	8700(5)	359(21)
C(51)	4353(10)	2496(5)	8137(6)	430(24)
C(12)	1976(7)	7432(5)	6118(5)	278(18)
C(22)	1854(9)	9329(5)	5816(6)	411(23)
C(32)	1474(9)	8989(5)	6886(5)	377(22)
C(42)	1197(9)	7105(5)	8130(5)	367(21)
C(52)	2629(10)	8343(6)	4190(5)	462(25)

Structural results are in good agreement with the FT-IR and FT-Raman spectroscopic data. The Raman peaks around 230 ± 10 and 193 ± 5 cm^{-1}, observed in all compounds (Table 8), should contain a high contribution of the ν(Se−Se) vibration, and as expected on the basis of the Se−Se bond lengthening, they fall at frequencies lower than that of 251 cm^{-1} reported for ν(Se−Se) in pure Se_8.[41] In accordance with this assignment, the corresponding FT-IR bands are very low in intensity, except for **III** and **IV**, where they fall at 199 cm^{-1} in **III** as a very strong unique broad absorption and at 229 s and 195 ms cm^{-1} in **IV** (Table 8). The enhanced intensities of the infrared bands observed in **III** and **IV** could be explained by the strong interaction of Se(11) and Cl^- and Br^- respectively.

The Raman spectrum of **III** having the strongest peak at 115 cm^{-1} and a weak one at 139 cm^{-1} is in accordance with the presence of an asymmetric I_3^-.[42] The same is observed in **V**,

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Table 8. Far FT-IR[a] and FT-Raman[b] Bands (cm^{-1}) of All Reported Compounds

compound	mode of observn	ν(Se−Se)	polyhalide[e]			assignt	other bands between 300 and 80 cm^{-1}
			ν_1	ν_2	ν_3		
$(C_5H_8N_2Se-)_2Br_2$ (**I**)	Raman	230 (10)−198 (4.6)					279 (1.3), 259 (3.8), 99 (1.0), 80 (1.8)
	IR	234 sh−197 w					289 s, 255 ms, 90 vsb
$(C_5H_8N_2Se-)_2I_2$ (**II**)	Raman	221 (10)−195 (8.0)					278 (0.6), 257 (2.0), 142 (0.2), 96 (0.8), 80 (0.9)
	IR	227 w−198 w					289 s, 254 ms, 170 m, 146 w, 131 w, 110 w
$[(C_5H_8N_2Se-)_2Cl]I_3$ (**III**)	Raman	229 (1.8)−193 (1.5)	115 (10)	89 (0.9)	139 (0.9)	I_3^-	276 (0.3), 261 (0.4)
	IR	199 vsb	129 vsb		129 vsb	I_3^-	288 ms, 261 m
$[(C_5H_{10}N_2Se-)_2Br]IBr_2$ (**IV**)[c]	Raman	240 (1.3)−193 (2.2)	157 (3.3)		193 (2.2)	IBr_2^-	
			132 (9.2)			I_2Br^-	
			115 (10)			I_3^-	
	IR	229 s−195 ms	157 ms		195 ms	IBr_2^-	170 w, 86 w
			117 msb			I_3^-, I_2Br^-	
$(C_5H_7N_2Se-)_2I_3\cdot{}^1/_2I_4$ (**V**)[d]	Raman	227 (5.7)−189 (0.7)	155 (10)			I_2 in I_4^{2-}	283 (0.3)
			112 (9.5)		141 (4.8)	I_3^-	
	IR	226 mw−188 w	164 vw			I_2 in I_4^{2-}	280 m, 254 w, 91 w
					143 vsb	I_3^-	
$(C_5H_7N_2Se-)_2I_2$ (**VI**)	Raman	240 (10)−189 (1.3)					281 (0.4) + other very weak peaks
	IR	221 w−188 m					275 m, 249 w, 146 w, 131 w, 111 w, 83 vs

[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 assignments of IBr_2^-, I_2Br^- and I_3^-. [d] I_4^{2-} can be seen as a diiodine molecule lengthened by the interaction with two I^-. [e] ν_1 symmetrical stretching, ν_2 bending, and ν_3 antisymmetrical stretching.

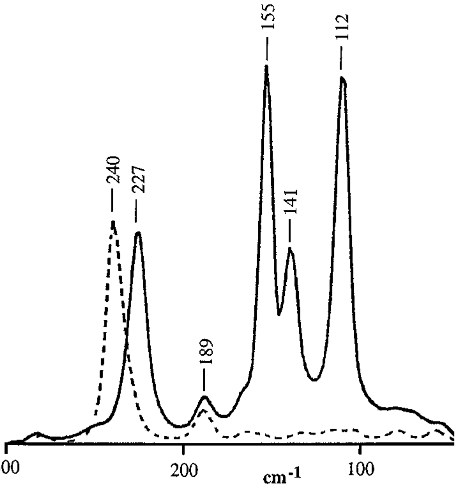

Figure 4. Superimposed FT-Raman spectra of **V** (—) and **VI** (- - -). The spectra have the same $[(C_5H_7N_2Se-)_2]^{2+}$ dication and different counterions (**V**; I_3^- and half I_4^{2-}; **VI**; two I^-).

where the peaks due to I_3^- fall at 112 cm^{-1} and 141 cm^{-1} (Figure 4); however, in the spectrum of **V** the most intense peak falls at 155 cm^{-1} and indicates the presence of a perturbed diiodine molecule, in good agreement with the structural features of the I_4^{2-} ion. In fact, the observed I−I bond distance [d(I−I) = 2.819(1) Å] and the ν(I−I) frequency at 155 cm^{-1} fall in the linear correlation ν(I−I)/d(I−I), found for numerous weak or medium−weak adducts with I_2.[43−44]

The FT-IR and FT-Raman spectra of **IV** appear to be more complex (Figure 5); once again, in the Raman spectrum, the peaks at 115, 132, and 157 cm^{-1} could be attributed to the symmetric and antisymmetric stretching of an I_3^- and to a perturbed diiodine molecule respectively. However the relative intensity of these peaks does not agree with this attribution, since the intensity of the peak 132 cm^{-1} is close to that of the peak at 115 cm^{-1} and the intensity of the peak at 157 cm^{-1} is lower than those of the other two. Moreover, it is important to point out that the peaks at 240 and 193 cm^{-1} (Figure 5) assigned to the prevailing contribution of the ν(Se−Se) vibration have reversed intensities with respect to those observed for all the other dications (Table 8). By considering the X-ray results, the Raman peaks at 115, 132, 157, and 193 cm^{-1} should contain contributions of the vibrational modes of the anions IBr_2^-, I_2Br^-, and I_3^-. In symmetric trihalides, only one vibrational mode is Raman active (symmetric stretching ν_1), while the other two (antisymmetric stretching ν_3 and deforming ν_2) are only infrared active;[42] in asymmetric trihalides, the three vibrations become active in both Raman and infrared spectroscopy. Consequently, for **IV**, we should expect nine different peaks both in the infrared and in the Raman spectra. The very large absorption observed between 110−170 cm^{-1} (see Figure 5) in the infrared spectrum of **IV** seems to be in agreement with this expectation, but it

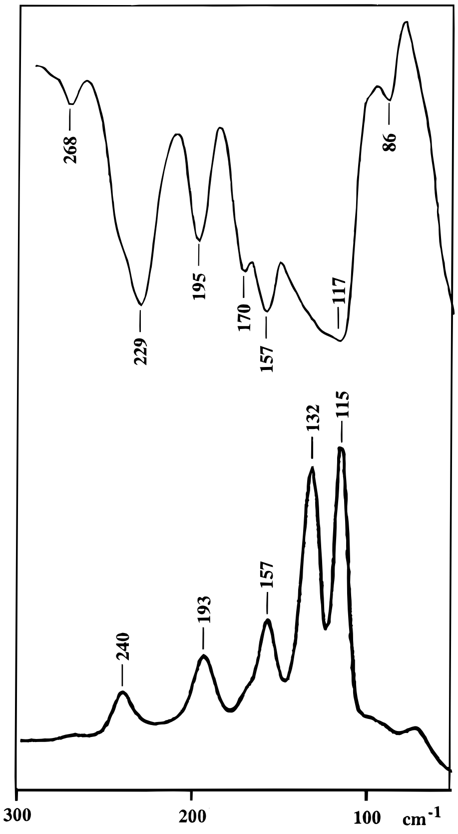

Figure 5. Superimposed FT-IR and FT-Raman spectra of **IV**.

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(43) Deplano, P.; Devillanova, F. A.; Ferraro, J. R.; Isaia, F.; Lippolis, V.; Mercuri, M. L. *Appl. Spectrosc.* **1992**, *46*, 1625.

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cannot be used to maky any attributions. Different from the well-studied Raman spectra of the I_3^- ions, a few Raman spectra related to IBr_2^- and I_2Br^- are reported in the literature.[7,45−47] Apart from some discrepancies,[47] the reported assignments for IBr_2^- are as follows: ν_1 ranges between 143 and 168 cm^{-1}, ν_3 falls between 178 and 184 cm^{-1}, and the deforming ν_2 falls lower than 98 cm^{-1}. The assignments for I_2Br^- have been carried out by Ferraro *et al*.[47] who reported values around 130, 112, and 70−80 cm^{-1}, both in the Raman spectrum and in the infrared spectrum for $(n\text{-Bu})_4NI_2Br$. Taking into account the previous attributions, the peak at 157 cm^{-1} should contain the prevailing contribution of the ν_1 vibration of IBr_2^-; its antisymmetric stretching ν_3 should contribute to the peak at 193 cm^{-1}, which is mainly attributed to the ν(Se−Se) vibration. The other two Raman peaks at 132 and 115 cm^{-1} should contain prevailing contributions of the vibrations related to I_2Br^- and I_3^- respectively.

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Supporting Information Available: Tables giving details of the crystallographic data collection (compounds **I**−**V**) positional and thermal parameters (compounds **IV**), calculated hydrogen atom parameters (compounds **I**−**V**), general displacement parameter expressions (compounds **I**−**V**) and interatomic distances and angles (compound **IV**) (19 pages). Ordering information is given on any current masthead page. Observed and calculated structure factor moduli are available from the authors.

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