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Conductivity, FT-Raman Spectra, and X-ray Crystal Structures of Two Novel $[D_2I]I_n$ (n = 3 and D = *N*-Methylbenzothiazole-2(3*H*)-selone; n = 7 and D = *N*-Methylbenzothiazole-2(3*H*)-thione) Iodonium Salts. First Example of $I^-\cdot 3I_2$ Heptaiodide

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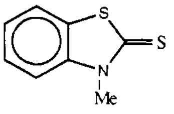
Solids of stoichiometry $\mathbf{1}\cdot 2I_2$ ($C_8H_7I_4NS_2$; **I**) and $\mathbf{2}\cdot I_2$ ($C_8H_7I_2NSSe$; **II**) are obtained respectively from mixtures of *N*-methylbenzothiazole-2(3*H*)-thione (**1**) and *N*-methylbenzothiazole-2(3*H*)-selone (**2**) with molecular diiodine in CH_2Cl_2 when the solutions were allowed to stand. The crystals of **I** are monoclinic (a = 9.445(1) Å, b = 18.233(2) Å, c = 18.673(2) Å, β = 98.62(1)°, Z = 4, space group $P2_1/c$; R = 0.030) and consist of the $[(\mathbf{1})_2I]^+$ cations and I_7^- anions, formed by interaction of I^- with three diiodine molecules (short distances ranging between 2.746 and 2.771 Å, long distances between 3.237 and 3.260 Å). The I_7^- anions interact weakly with each other (3.502 Å) to form parallel chains of anions; the cations are located between these chains. The crystals of **II** are triclinic (a = 12.147(10) Å, b = 9.681(4) Å, c = 10.950(4) Å, α = 71.03(2)°, β = 93.93(2)°, γ = 99.14(2)°, Z = 1, space group $P\bar{1}$; R = 0.027) and consist of $[(\mathbf{2})_2I]^+$ cations and triiodide anions located on different crystallographic centers (d(I–I) = 2.899 and 2.919 Å for the two differently positioned triiodides). The FT-Raman spectra in the characteristic ν(I–I) region show a very strong band for compound **II** at 121.2 cm^{-1}, in accordance with the presence of a symmetrical triiodide anion, while for **I** the medium peak at 175.2 cm^{-1} and the strong one at 157.4 cm^{-1} are indicative of the presence of perturbed diiodine molecules, as generally found in donor–I_2 adducts of weak or medium-weak strength. Both compounds have very low electric conductivity.

Introduction

Recently,[2] we reported the FT-Raman spectra of some polyiodides and a series of $D\cdot I_2$ charge-transfer (CT) complexes (where D is a donor containing the thione or selone group), previously characterized by X-ray diffraction studies, with the aim of testing the ability of FT-Raman spectroscopy in identifying the nature of the iodine. In fact, Raman spectroscopy has been widely used for this purpose in the past few years.[3-9] For all of the considered adducts between the sulfur compounds and diiodine, we found that FT-Raman frequencies ν(I–I) can be correlated linearly with the d(I–I) bond distances. As the interiodine distance increases on complex formation, the stretching vibration moves to a lower frequency with respect to the value reported for the solid diiodine.[10] This seems to occur not only for the sulfur adducts but also for all the compounds in which the diiodine unit can be considered to be a perturbed diatomic molecule, i.e. for weak or medium-weak complexes, irrespective of the nature of the donor atom. We proposed a criterion to differentiate strong complexes from weak or medium-weak complexes,[2] based on the value of the I–I bond order, calculated as a function of the I–I bond lengthening, according to the equation proposed by Pauling.[11,12] If the interaction does not reduce the I–I bond order below 0.6, the diiodine may still be considered a perturbed diatomic molecule irrespective of the donor type, and one may expect to see one FT-Raman band shifted to a lower frequency. The validity of this hypothesis is supported by the fact that very asymmetric triiodides, pentaiodides, or charge-transfer complexes with thioketonic sulfur give very similar FT-Raman spectra.[2] When the interaction between a donor and diiodine is very strong (i.e. I–I bond order lower than 0.6), as in the case of adducts with selonic selenium[13] or in symmetric triiodide,[2] a three-body system must be taken into account to predict the Raman peaks.[14] We concluded that in order to support better our preliminary findings, more FT-Raman data on structurally characterized neutral adducts of different strengths or polyiodides were necessary.[15]

For this reason, we undertook a systematic preparation of crystalline compounds by reacting diiodine with different donors, all containing the thio- or selenoamido group. The D donors considered in this paper are *N*-methylbenzothiazole-2(3*H*)-thione (**1**) and *N*-methylbenzothiazole-2(3*H*)-selone (**2**). In contrast



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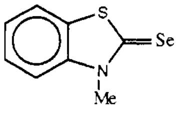

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Table I. Crystallographic Data

	$[1_2I][I{\cdot}3I_2]$ (I)	$[2_2I][I_3]$ (II)
formula	$C_{16}H_{14}I_8N_2S_4$	$C_{32}H_{28}I_8N_4S_4Se_4$
fw	1377.79	1927.94
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.445(1)	12.147(10)
b (Å)	18.233(2)	9.681(4)
c (Å)	18.673(2)	10.950(4)
α (deg)	90	71.03(2)
β (deg	98.62(1)	93.93(2)
γ (deg)	90	99.14(2)
V (Å^3)	3179(1)	1202(1)
Z	4	1
D_{calcd} (g cm^{-3})	2.878	2.654
μ(Mo Kα) (cm^{-1})	79.89	82.76
Final R and R_w indices[a]	0.030, 0.041	0.027, 0.037

[a] $R = [\sum(F_o - kF_c)/\sum F_o]$; $R_w = [\sum w(F_o - kF_c)^2/\sum wF_o^2]^{1/2}$; $w = 1/(\sigma(F_o))^2$; $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oLp$.

to what was found in the CH_2Cl_2 solution,[16] the crystalline solids obtained by reacting **1** and **2** with molecular diiodine were ionic salts as described in this paper.[17]

Experimental Section

Preparation of Compound I. This compound was obtained from a dichloromethane solution of *N*-methylbenzothiazole-2(3*H*)-thione (**1**) and diiodine in a 1:1 molar ratio in air at 4 °C. After several days a brown dust and only one crystal with a green metallic luster were obtained. On the basis of the stoichiometry of this crystal ($\mathbf{1}{\cdot}2I_2$) we repeated the preparation using a 1:2 molar ratio. After the mixture was allowed to stand overnight at 4 °C, the desired compound was formed quantitatively as crystals with a green metallic luster. Anal. Found (calcd for $C_8H_7I_4NS_2$): C, 14.05 (13.95); H, 0.97 (1.02); N, 2.11 (2.03); S, 9.44 (9.31).

Preparation of Compound II. This compound was obtained from a dichloromethane solution of *N*-methylbenzothiazole-2(3*H*)-selone (**2**) and diiodine in a 1:1 molar ratio in air at 4 °C. After 2 days, black crystals with a violet metallic luster were formed. Anal. Found (calcd for $C_8H_7I_2NSSe$): C, 20.17 (19.94); H, 1.36 (1.46); N, 2.97 (2.91); S, 6.94 (6.65).

X-ray Data Collection and Structure Determination. Crystal data and other experimental details are summarized in Table I. The crystals used were coated with cyanoacrylate glue to prevent loss of diodine during the data collection; nevertheless, a maximum decay of 28% and 7% evaluated on F_o was observed for **I** and **II**, respectively. The diffraction experiments were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The diffracted intensities were corrected for Lorentz factors, polarization, decay, and absorption (empirical correction)[18] and for extinction (extinction correction $F_c/(1 + glc)$ with $g = 6.6 \times 10^{-8}$ and 3.3×10^{-7} for **I** and **II** respectively). Scattering factors for all the atomic species and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from ref 19. Both structures were solved by direct methods (MULTAN)[20] and refined by full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - k|F_c|)^2$. An anisotropic thermal parameter was assigned to all the non-hydrogen atoms. The hydrogen atoms were introduced into the structure model at calculated positions (C–H 0.95 Å) with the exception of those of the methyl groups which were seen in a difference Fourier map; no refinement was attempted for these atoms. The final difference Fourier synthesis showed maxima residuals of 1.3 e/Å^3 for **I** and 0.8 e/Å^3 for **II** close to the iodine atoms. The final atomic coordinates are listed in Tables II and III. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[21]

Table II. Fractional Atomic Coordinates of the Non-Hydrogen Atoms for Compound $[(\mathbf{1})_2I]^+I_7^-$ (**I**) with Esd's in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
I(1)	0.59822(5)	0.21103(3)	0.73721(3)	4.03(1)
I(2)	0.93507(5)	0.19555(3)	0.72465(3)	3.53(1)
I(3)	1.22885(6)	0.18477(4)	0.72901(3)	4.33(1)
I(4)	0.63100(6)	0.03317(3)	0.74653(3)	4.20(1)
I(5)	0.67893(9)	−0.11539(4)	0.74796(4)	6.22(2)
I(6)	0.48262(7)	0.25757(4)	0.57117(3)	4.93(1)
I(7)	0.3865(1)	0.28779(5)	0.42689(4)	7.52(2)
I(8)	0.79181(6)	0.41681(3)	0.73949(3)	4.41(1)
S(11)	1.0559(3)	0.4978(1)	0.8640(1)	4.44(5)
S(12)	0.8975(3)	0.3532(1)	0.8604(1)	6.16(6)
S(21)	0.9610(2)	0.5474(1)	0.6433(1)	3.92(4)
S(22)	0.6760(2)	0.4699(2)	0.6130(1)	5.52(6)
N(11)	1.0947(8)	0.4037(4)	0.9655(3)	4.2(1)
N(21)	0.8064(7)	0.5458(4)	0.5191(3)	3.7(1)
C(11)	1.1898(9)	0.4605(5)	0.9897(4)	4.1(2)
C(12)	1.283(1)	0.4644(6)	1.0537(5)	5.6(2)
C(13)	1.368(1)	0.5263(6)	1.0668(5)	6.6(3)
C(14)	1.362(1)	0.5815(6)	1.0173(5)	5.6(2)
C(15)	1.271(1)	0.5771(5)	0.9528(5)	4.9(2)
C(16)	1.1833(9)	0.5170(5)	0.9387(4)	4.0(2)
C(17)	1.0168(9)	0.4154(5)	0.9007(4)	4.0(2)
C(18)	1.079(1)	0.3390(5)	1.0087(5)	6.1(2)
C(21)	0.9226(9)	0.5910(4)	0.5100(4)	3.6(2)
C(22)	0.948(1)	0.6251(5)	0.4476(4)	5.1(2)
C(23)	1.070(1)	0.6671(6)	0.4509(5)	5.6(2)
C(24)	1.167(1)	0.6742(5)	0.5143(5)	5.3(2)
C(25)	1.1407(9)	0.6402(5)	0.5769(5)	4.4(2)
C(26)	1.0205(8)	0.5966(5)	0.5742(4)	3.7(2)
C(27)	0.8089(8)	0.5202(4)	0.5871(4)	3.5(2)
C(28)	0.687(1)	0.5319(6)	0.4619(5)	6.0(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 III. Fractional Atomic Coordinates of the Non-Hydrogen Atoms for Compound $[(\mathbf{2})_2I]^+I_3^-$ (**II**) with Esd's in Parentheses

atom	x	y	z	B_{eq},[a] Å^2
I(1)	0.16394(3)	0.39557(4)	0.21051(3)	3.524(8)
I(2)	0.500	0.500	0.000	3.37(1)
I(3)	0.62595(4)	0.25501(5)	0.05911(4)	4.97(1)
I(4)	−0.14570(4)	0.22728(5)	0.43152(4)	4.53(1)
I(5)	0.000	0.000	0.500	3.59(1)
Se(11)	0.19167(6)	0.37026(7)	0.47249(5)	4.50(1)
Se(21)	0.13148(5)	0.42614(6)	−0.04456(5)	3.62(1)
S(11)	0.3485(1)	0.6471(2)	0.3053(1)	3.98(3)
S(21)	−0.0444(1)	0.1689(2)	0.1219(1)	3.53(3)
N(11)	0.3657(4)	0.5576(5)	0.5496(4)	3.02(9)
N(21)	−0.0356(4)	0.2306(5)	−0.1210(4)	3.19(9)
C(11)	0.4471(4)	0.6816(6)	0.5113(5)	3.0(1)
C(12)	0.5204(5)	0.7408(7)	0.5910(5)	4.3(1)
C(13)	0.5941(6)	0.8645(7)	0.5307(6)	5.0(2)
C(14)	0.5952(6)	0.9291(7)	0.3996(6)	5.0(2)
C(15)	0.5218(5)	0.8716(7)	0.3203(6)	4.5(1)
C(16)	0.4480(5)	0.7468(6)	0.3787(5)	3.7(1)
C(17)	0.3060(5)	0.5257(6)	0.4528(4)	3.4(1)
C(18)	0.3446(5)	0.4735(7)	0.6844(5)	4.3(1)
C(21)	−0.1225(4)	0.1112(6)	−0.0835(5)	3.1(1)
C(22)	−0.1915(5)	0.0470(6)	−0.1634(5)	4.2(1)
C(23)	−0.2733(5)	−0.0668(7)	−0.1044(6)	4.9(2)
C(24)	−0.2879(5)	−0.1151(7)	0.0258(6)	4.7(2)
C(25)	−0.2212(5)	−0.0499(6)	0.1051(5)	4.0(1)
C(26)	−0.1377(4)	0.0639(6)	0.0486(5)	3.2(1)
C(27)	0.0143(4)	0.2720(5)	−0.0233(4)	2.9(1)
C(28)	−0.0021(6)	0.3009(7)	−0.2570(5)	4.7(1)

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

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(15) The interpretation of the FT-Raman spectra of iodine-rich compounds seems to be more complicated, since we have also found that the structural parameters of I_3^- (2.969–2.871 Å) in *o*-(diphenylphosphino)hydroxophenyl, *o*-(diphenylphosphino)oxophenyl, and phenylphosphine oxide triiodide are very similar to those reported for 5,5-dimethyl-2-(methylthio)-4-oxoimidazolidinium triiodide (2.995–2.885 Å), but the two compounds show different FT-Raman spectra (ref 2).

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Table IV. Selected Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses[a]

	$[(\mathbf{1})_2\mathrm{I}]^+\mathrm{I}_7^-$ (**I**)	$[(\mathbf{2})_2\mathrm{I}]^+\mathrm{I}_3^-$ (**II**)		$[(\mathbf{1})_2\mathrm{I}]^+\mathrm{I}_7^-$ (**I**)	$[(\mathbf{2})_2\mathrm{I}]^+\mathrm{I}_3^-$ (**II**)
(a) Within the Cation					
I(8)–S(12)	2.600(2)		Se(11)–I(1)–Se(21)		178.02(2)
I(8)–S(22)	2.634(2)		I(1)–Se(11)–C(17)		96.7(1)
I(1)–Se(11)		2.800(1)	Se(11)–C(17)–N(11)		124.9(4)
I(1)–Se(21)		2.719(1)	Se(11)–C(17)–S(11)		123.4(3)
Se(11)–C(17)		1.845(5)	S(12)–I(8)–S(22)	174.97(7)	
S(12)–C(17)	1.694(7)		I(8)–S(12)–C(17)	103.3(2)	
C(17)–N(11)	1.336(9)	1.335(5)	S(12)–C(17)–N(11)	122.4(5)	
N(11)–C(11)	1.401(9)	1.396(6)	S(12)–C(17)–S(11)	125.3(4)	
N(11)–C(18)	1.449(9)	1.453(6)	S(11)–C(17)–N(11)	112.3(5)	111.8(4)
C(17)–S(11)	1.716(7)	1.716(5)	C(17)–N(11)–C(11)	114.5(6)	114.6(4)
S(11)–C(16)	1.736(7)	1.743(5)	N(11)–C(11)–C(16)	111.4(6)	112.0(4)
C(11)–C(16)	1.398(9)	1.382(6)	C(11)–C(16)–S(11)	110.7(6)	110.4(4)
C(11)–C(12)	1.373(10)	1.393(7)	C(16)–S(11)–C(17)	91.1(3)	91.2(2)
C(12)–C(13)	1.387(12)	1.377(8)	C(17)–N(11)–C(18)	123.1(7)	122.7(4)
C(13)–C(14)	1.361(12)	1.366(8)	C(11)–N(11)–C(18)	122.4(6)	122.6(4)
C(14)–C(15)	1.373(10)	1.381(8)	I(1)–Se(21)–C(27)		96.3(1)
C(15)–C(16)	1.374(10)	1.380(7)	Se(21)–C(27)–S(21)		124.5(2)
Se(21)–C(27)		1.858(5)	Se(21)–C(27)–N(21)		123.5(3)
S(22)–C(27)	1.682(7)		I(8)–S(22)–C(27)	103.3(2)	
C(27)–N(21)	1.352(8)	1.336(5)	S(22)–C(27)–N(21)	123.4(5)	
N(21)–C(21)	1.402(9)	1.408(6)	S(22)–C(27)–S(21)	125.0(4)	
N(21)–C(28)	1.454(8)	1.477(6)	S(21)–C(27)–N(21)	111.6(5)	112.0(3)
C(27)–S(21)	1.720(6)	1.711(5)	C(27)–N(21)–C(21)	114.4(5)	114.3(4)
S(21)–C(26)	1.732(7)	1.733(5)	N(21)–C(21)–C(26)	111.6(6)	111.5(4)
C(21)–C(26)	1.404(9)	1.383(6)	C(21)–C(26)–S(21)	110.6(5)	110.9(4)
C(21)–C(22)	1.374(9)	1.394(6)	C(26)–S(21)–C(27)	91.8(3)	91.4(2)
C(22)–C(23)	1.382(12)	1.377(8)	C(27)–N(21)–C(28)	123.3(6)	123.5(4)
C(23)–C(24)	1.388(11)	1.363(8)	C(21)–N(21)–C(28)	122.7(6)	122.2(4)
C(24)–C(25)	1.378(10)	1.381(7)			
C(25)–C(26)	1.381(9)	1.383(7)			
(b) Within the Iodine Atoms of I_7^- or I_3^-					
I(1)–I(2)	3.237(1)		I(1)–I(2)–I(3)	174.15(2)	
I(1)–I(4)	3.260(1)		I(1)–I(4)–I(5)	174.94(2)	
I(1)–I(6)	3.242(1)		I(1)–I(6)–I(7)	176.23(2)	
I(1)···I(3)[a]	3.502(1)		I(2)–I(1)–I(4)	80.25(2)	
I(2)–I(3)	2.771(1)	2.899(1)	I(2)–I(1)–I(6)	98.47(2)	
I(4)–I(5)	2.746(1)	2.919(1)	I(4)–I(1)–I(6)	109.09(2)	
I(6)–I(7)	2.766(1)		I(2)–I(1)···I(3)[a]	165.52(2)	
			I(3)–I(2)–I(3)[b]		180
			I(4)–I(5)–I(4)[c]		180

[a] Symmetry codes: (a) $x - 1, y, z$; (b) $1 - x, 1 - y, -z$; (c) $-x, -y, 1 - z$.

FT-Raman Spectra. The FT-Raman spectra (resolution ±4 cm^{-1}) were recorded on an FRA 106 FT-Raman accessory mounted on a Bruker IFS 66 FT-IR vacuum instrument operating with an exciting frequency of 1064 nm (Nd:YAG laser) and with a germanium diode detector cooled at liquid N_2 temperature. Power levels of laser source varied between 20 and 100 mW. The solid samples were packed into a suitable cell and then fitted into the compartment designed for use 180° scattering geometry. No sample decomposition was observed during the experiments.

Conductivity Measurements. The conductivity measurements were made on pressed disks with a thickness in the range 2–4 mm and a diameter of 13 mm, made with a Spectratech die and a hydraulic press using a pressure of 10 tons. Great care must be taken in handling the disks to avoid damage prior to conductivity measurement.

A Time Electronics Ltd D.C 0–10V voltage calibrator (type 2003S 0.02% grade) in conjunction with a ×100 voltage multipler was used as the reference voltage source, and current was measured using a Keithley instruments Model 410A picoammeter. Both four-point and two-point probe methods were used for the conductivity measurements;[22] the two-point probe was prefered for the more fragile samples.

Results

Structure of Compound I. The fractional atomic coordinates of compound $\mathbf{1}\cdot 2\mathrm{I}_2$ (**I**) (**1** = *N*-methylbenzothiazole-2(3*H*)-thione) are reported in Table II; the selected interatomic distances and angles are shown in Table IV. The crystals of compound **I** contain $[(\mathbf{1})_2\mathrm{I}]^+$ cations and I_7^- anions with interactions between cations and anions not shorter than the sum of van der Waals radii.

The cation consists of two ligand molecules of *N*-methylbenzothiazole-2(3*H*)-thione coordinated with the I^+ ion (see Figure 1); the S–I–S arrangement is almost linear (174.97(7)°) and is slightly asymmetric (2.600(2) and 2.634(2) Å).

The I_7^- anions and their packing show interesting features (see Figure 2). Each anion is made up of three diiodine molecules interacting with a single I^- ion. In these three molecules the I–I distances (in the range 2.746(1)–2.771(1) Å) are typical of a weakly perturbed diiodine, whereas the interactions with the I^- ion are longer and range from 3.237(1) to 3.260(1) Å. The I_7^- ions, repeated along the [100] direction by a translation equal to the *a* unit cell parameter, are separated only by 3.502(1) Å, thus giving rise to infinite $(\mathrm{I}_7)_n^{n-}$ polyiodide chains. The $[(\mathbf{1})_2\mathrm{I}]^+$ cations are located in the channels between these polyiodide chains running along [100]. For reasons of clarity, only the iodine atom is reported in Figure 2 instead of the $[(\mathbf{1})_2\mathrm{I}]^+$ cation.

Structure of Compound II. The fractional atomic coordinates of compound $\mathbf{2}\cdot\mathrm{I}_2$ (**II**) (**2** = *N*-methylbenzothiazole-2(3*H*)-selone) are reported in Table III; the selected interatomic distances and angles are shown in Table IV. The crystals of compound **II** contain $[(\mathbf{2})_2\mathrm{I}]^+$ cations and two symmetric I_3^- anions with interactions between cations and anions not shorter than the sum of van der Waals radii.

The cation consists of two ligand molecules of *N*-methylbenzothiazole-2(3*H*)-selone coordinated with the I^+ ion (see Figure 3); also, the Se–I–Se arrangement is practically linear (178.02(2)°) and asymmetric (2.800(1) and 2.719(1) Å).

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[22] *Low Level Measurements*; *3rd ed.*, Keithley Instruments: Cleveland, OH, 1984.

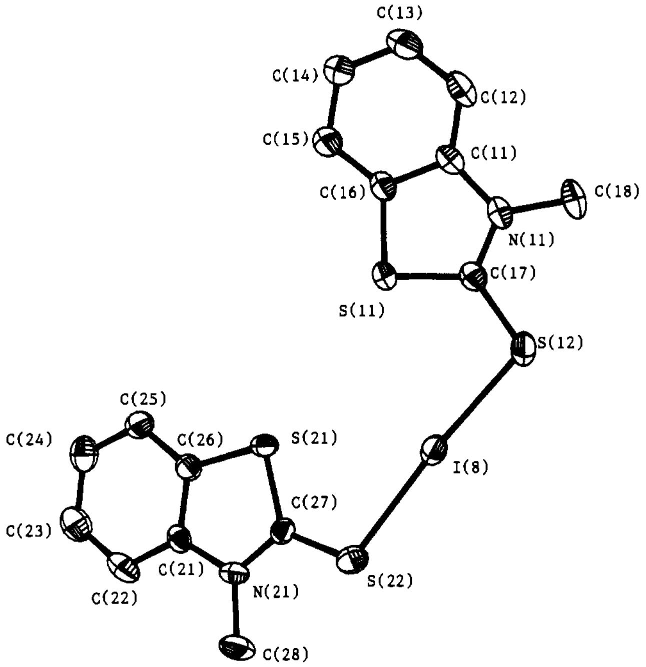

Figure 1. ORTEP view of the bis(*N*-methylbenzothiazolyl-2-thio)iodonium cation. Thermal ellipsoids are drawn at the 30% probability level.

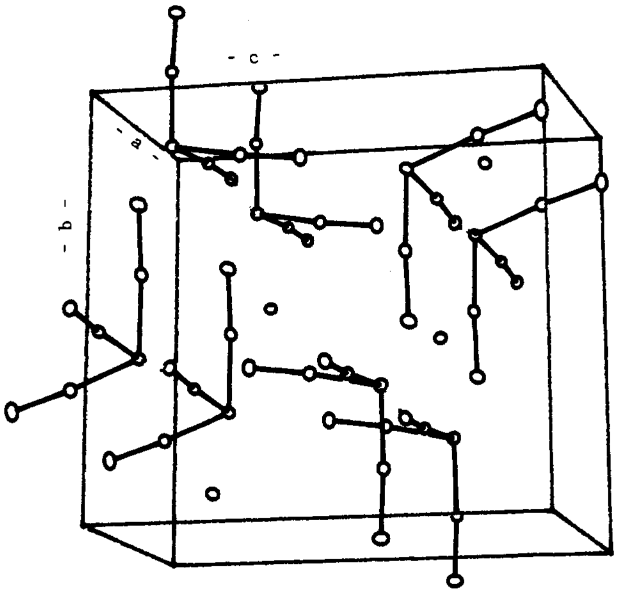

Figure 2. Crystal packing of the I_7^- anions. For clarity, instead of the $[(\mathbf{1})_2I]^+$ cation, only the iodine atom is reported.

The unit-cell of compound **II** (see Figure 4) contains two centrosymmetrically related $[(\mathbf{2})_2I]^+$ cations in a general position of the space group and two I_3^- located on two different crystallographic inversion centers. In the two independent symmetric I_3^- anions slightly different distances are observed: 2.899(1) and 2.919(1) Å.

FT-Raman Spectra and Conductivity Measurements. The superimposed FT-Raman spectra of **I** and **II** are reported in Figure 5. In both spectra, the bands attributable to the stretching vibrations of the iodine atoms dominate all the other Raman bands due to the organic molecule. The FT-Raman spectrum of **I** shows a very strong peak at 157.4 cm^{-1} with an overtone at 317.1 cm^{-1} and a medium peak at 175.2 cm^{-1}. The spectrum of **II** is characterized by a very strong peak at 121.2 cm^{-1} and a medium peak at 207.1 cm^{-1}. Other very weak peaks are present below 500 cm^{-1}, but none of these could be identified positively as a combination band or overtone.

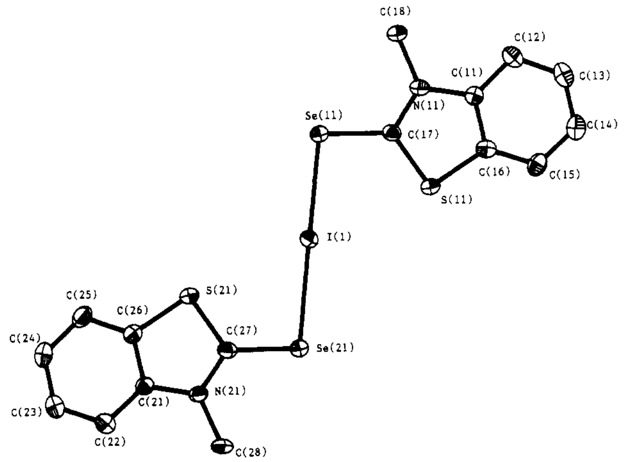

Figure 3. ORTEP view of the bis(*N*-methylbenzothiazolyl-2-seleno)iodonium cation. Thermal ellipsoids are drawn at the 30% probability level.

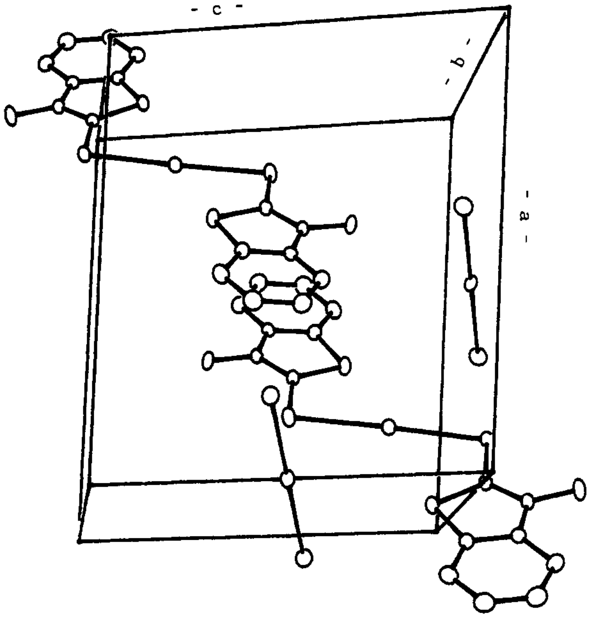

Figure 4. Crystal packing of bis(*N*-methylbenzothiazolyl-2-seleno)iodonium triiodide. The unit-cell contains two centrosymmetrically related $[(\mathbf{2})_2I]^+$ cations in a general position of the unit cell and two I_3^- located on two different crystallographic inversion centers.

The conductivity of the two compounds is very low; the highest values recorded were 2×10^{-10} and 4×10^{-10} Ω^{-1} cm^{-1} for **I** and **II** respectively.

Discussion

As shown by X-ray structural results, the crystalline compounds of $\mathbf{1}\cdot 2I_2$ and $\mathbf{2}\cdot I_2$ are surprisingly ionic compounds and not molecular adducts as found in CH_2Cl_2 solutions.[16] Both compounds contain I^+ acting as a metal ion to form the $[D_2I]^+$ cation (D = **1** and **2**). Only a few structures of this kind have been reported until now[23-27] and to our knowledge the bis(*N*-methylbenzothiazole-2(3*H*)-selone) iodonium cation is the first example with a Se donor atom.

Data for some previously reported iodonium cations are shown in Table V, together with the structural parameters of the X–I–X framework. The comparison between $[(\mathbf{1})_2I]^+$ with $[(\mathrm{tu})_2I]^+$ (tu

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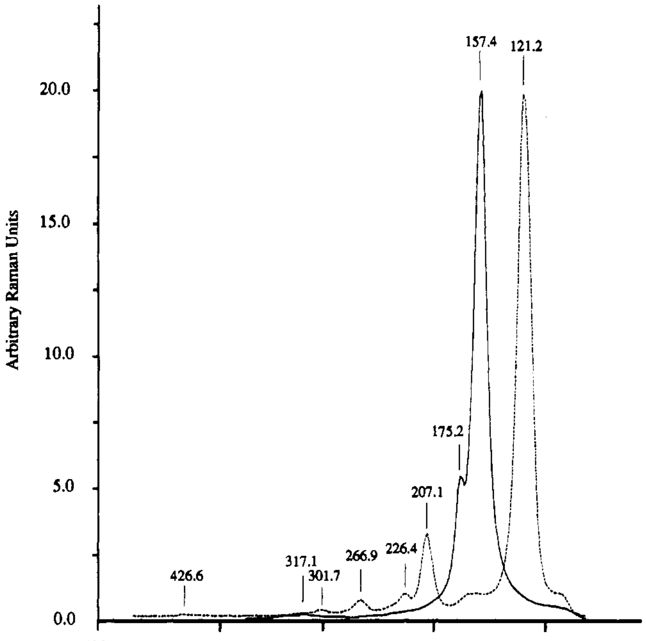

Figure 5. Superimposed FT-Raman spectra of bis(*N*-methylbenzothiazolyl-2-thio)iodonium heptaiodide (—) and bis(*N*-methylbenzothiazolyl-2-seleno)iodonium triiodide (···).

Table V. Structural Parameters of Known $[D_2I]^+$ Iodonium Cations[a]

compd	X	X- - -I- - -X (Å)	(Å)	∠X-I-X (deg)	ref
$[(HMT)_2I]^+$	N	2.30	2.30	176.5	24
$[(py)_2I]^+$	N	2.16	2.16		25
$[(tu)_2I]^+$	S	2.629	2.629	180.0	23
$[(thiol)_2I]^{5+}$	S	2.619(2)	2.619(2)	173.1	26
$[(S_7I)_2I]^{3+}$	S	2.674(7)	2.674(7)	180	27
$[(\mathbf{1})_2I]^+$	S	2.634(2)	2.600(2)	174.97(7)	this work
$[(\mathbf{2})_2I]^+$	Se	2.719(1)	2.800(1)	178.02(2)	this work

[a] Key HMT = hexamethylenetetramine; tu = thiourea; py = pyridine; $[thiol]^{2+}$ = bis(ethylenediamine)(ethyleneaminethiolato)cobalt(2+); $[S_7I]^+$ = 4-iodocycloheptasulfur(1+); **1** = *N*-methylbenzothiazole-2(3*H*)-thione; **2** = *N*-methylbenzothiazole-2(3*H*)-selone.

= thiourea), $[(thiol)_2I]^{5+}$ ($[thiol]^{2+}$ = bis(ethylenediamine)-(ethyleneaminethiolate)cobalt(2+)) and $[(S_7I)_2I]^{3+}$ ($[S_7I]^+$ = 4-iodocycloheptasulfur(1+)) shows that the S–I bond lengths are very close, although in $[(\mathbf{1})_2I]^+$ the S–I–S framework is not symmetric. The S–I distance of 2.600(2) Å is one of the shortest bonds reported in literature[28,29] and is similar to that found in the α and β forms of 1,3-dimethylimidazole-2-thione·I_2 (2.616 and 2.607 Å respectively[30]). The bond distances and angles in the two coordinated organic molecules are very similar; the comparison between these values and those reported by Wheatley[31] on *N*-methylbenzothiazole-2(3*H*)-thione shows that the coordination with I^+ lengthens the C=S bond and at same time shortens the N—C(=S)—S bonds of the pentaatomic ring. (This comparison is only indicative, since the structural determination of *N*-methylbenzothiazole-2(3*H*)-thione is not very accurate).

The Se–I–Se framework of the bis(*N*-methylbenzothiazole-2(3*H*)-selone) iodonium cation is practically linear and fairly asymmetric. Apart from the C=Se bond length, all the other distances and angles of the organic molecules are very similar to those of *N*-methylbenzothiazole-2(3*H*)-thione. Very few data on the Se–I bond distances are reported in the literature; however, the length in the present cation is comparable to those reported for 1,4-diselenane·$2I_2$ (2.829(4) Å[32]), tetrahydroselenophene·I_2 (2.762(5) Å[33]), and 1-oxa-4-selenacyclohexane·I_2 (2.755(4) Å[34]), but longer than those reported for 5,5-dimethyl-4-oxoimidazolidine-2-selone (2.699(1) Å[13]), 1-oxa-4-selenacyclohexane·ICI (2.63(5) Å[35]), and phenyl iodoselenide (2.529 Å[36]). The Se–I bond distance in the cyclic dimer of diphenyldiselenane·I_2 is 2.992 Å.[37]

Until 1992, only two solid-state structures, $[NEt_4]^+I_7^-$ and $[(py)_2I]^+I_7^-$, were reported for the heptaiodide ion.[24,38] Both structures show the same two-dimensional network of symmetrical I_3^- ions joined by I_2 units. Very recently, Poli and co-workers[39] reported the crystal structure of $[PPh_4]^+I_7^-$ as the first discrete structure for the I_7^- ion, again describable as an I_3^- Lewis base interacting with two I_2 acceptors ($I_3^-{\cdot}2I_2$). In the $[PPh_4]^+I_7^-$ salt, the I_3^- unit is significantly asymmetric (2.814(1), 3.057(1) Å) and slightly longer (5.871 Å) than the symmetrical ones (5.84 Å). As described in the results, our I_7^- ion differs from that reported by Poli in the fact that it is formed by an I^- interacting with three I_2 acceptors ($I^-{\cdot}3I_2$); in fact, the I–I distances in the three I_2 units range between 2.746(1) and 2.771(1) Å, whereas the three $I^-{\cdots}I_2$ distances range between 3.237(1) and 3.260(1) Å. This is the first example of the I_7^- ion describable as $I^-{\cdot}3I_2$. Heptaiodides describable as $I^-{\cdot}3I_2$ and $I_5^-{\cdot}I_2$ have been hypothesized,[40] but only the latter was considered the better model for the interpretation of the Raman spectra of N-alkylurotropinium heptaiodides ($RUrI_7$). In comparison with the other three structures reported in the literature, the I_7^- ion of the $[PPh_4]^+I_7^-$ salt can be considered an intermediate situation between these two extremes, i.e. the cases of $[NEt_4]^+I_7^-$ and $[(py)_2I]^+I_7^-$, where a symmetric I_3^- exists, and the case of the present compound, where no I_3^- ion can be recognized.

The structural parameters are consistent with the observed FT-Raman spectra reported in Figure 5. The very strong band at 121.2 cm^{-1} in the triiodide compound is consistent with the symmetrical I_3^- ion, since the asymmetric stretching and the bending are Raman inactive.[4–9] In the case of I_7^- ion, two bands at 157.4 and 175.2 cm^{-1} dominate all the other Raman bands due to the organic molecule; their frequencies are in agreement with the conclusions drawn for the FT-Raman spectra of weak or medium-weak complexes of diiodine.[2] In fact, the simultaneous interaction of I^- with three different I_2 molecules slightly lengthens the I–I distances from 2.715 Å (measured in pure I_2[41]) to 2.746(1), 2.766(1) and 2.771(1) Å in the I_7^- anion. These slight lengthenings are indicative of I_2 adducts of medium–weak strength and one may expect the I_2 FT-Raman bands to be shifted to lower frequencies with respet to the value of 180 cm^{-1} found for solid I_2.[10] In agreement with this, the very strong band at 157.4 cm^{-1} could be assigned to the two I_2 with longer distances (2.766(1) and 2.771(1) Å) and the medium band at 175.2 cm^{-1} to that with the shorter I–I distance (2.746(1) Å). These frequencies fit fairly

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(28) Herbstein, F. H.; Schwotzer, W. *J. Am. Chem. Soc.* **1984**, *106*, 2367.

(29) S···I bond lengths shorter than those found in $[(\mathbf{1})_2I]^+$ have been reported in some charge transfer complexes of ethylenethiourea and dithizone: ethylenethiourea·$2I_2$ (2.487(3) Å), bis(dithizone)·$7I_2$ (2.506(8) Å), bis(ethylenethiourea)·$3I_2$ (2.580(7) Å) and 1-(1-imidazolin-2-yl)-2-thioxoimidazolinium triiodide—ethylenethiourea·I_2 (2.588(8) Å).[28]

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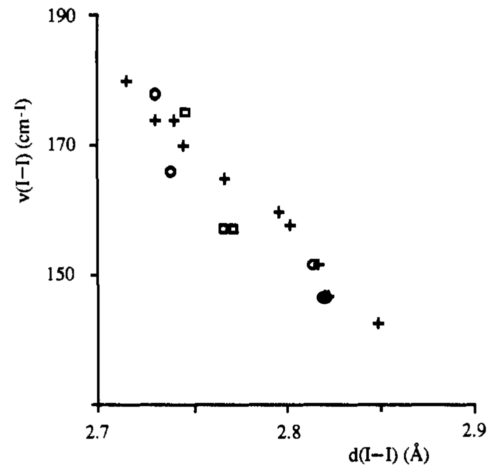

Figure 6. Linear correlation between the ν(I–I) FT-Raman bands for the weak or medium-weak complexes with I_2 versus d(I–I): (+) values taken from ref 2. The data obtained for the present heptaiodide (□) and that reported by ref 39 (○) fit fairly well with the correlation.

well with the linear correlation of ν(I–I) *versus* d(I–I) obtained for weak or medium–weak complexes with I_2 (see Figure 6).[42]

By comparison of the FT-Raman spectrum of the I_7^- ion under discussion with the resonance Raman spectrum of $[PPh_4]^+I_7^-$ reported by Poli,[39] it seems that in the FT-Raman case the I–I vibrations predominate the peaks due to the organic moiety (see Figure 5) better than in the resonance Raman, thus simplifying the attributions. However, in the $[PPh_4]^+I_7^-$ case, the observed bands at 178 and 166 cm^{-1} have been assigned "to the asymmetric stretches of the I···I–I units, with a large component from the strong I–I interaction" and the band at 152 cm^{-1} "to the asymmetric stretch of the I_3 unit." According to the discussion reported in ref 2, structural features suggest that, in this $I_7^-(I_3^-{\cdot}2I_2)$ ion, the I_3^- unit may still be considered an adduct ($I^-{\cdots}I_2$) of medium strength,[43] weakly interacting with the other two I_2. In this view, if the bands at 178 and 166 cm^{-1} are attributed to the weakly bonded I_2 and the band at 152 cm^{-1} to the I_2 of I_3^-, they correlate properly with the observed lengthening of the I–I distances (see Figure 6). According to the discussion reported in ref 42, the scatter from the linear correlation observed for the 178- and 166-cm^{-1} stretches could be explained, by the lowering of the C_s idealized symmetry of this $I_7^-(I_3^-{\cdot}2I_2)$ ion (normal modes of A′ + A″ type) to C_1 symmetry (2A). The consequent mixing of the two normal modes will raise the energy of the higher energy stretch and lower the energy of the lower energy stretch.

As far as the Raman spectrum of $[NEt_4]^+I_7^-$ is concerned,[44] it agrees well with the presence of a symmetrical I_3^- ($\nu \sim 110$ cm^{-1}). The band at ~180 cm^{-1} assigned to the coordinated I_2 falls outside the correlation and seems to agree better with an unbonded I_2.

The electric conductivity of both compounds at room temperature is very low; this is consistent with the absence of a continuous polyiodide chain in the structure of **I** and **II**. In the case of the heptaiodide, the parallel chains of the anions cannot be considered continuous because the sequence of localized I^- interacts weakly with the two I_2 molecules.

Conclusions

To conclude, we would like to make the following important points:

(i) The reaction products of **1** and **2** with I_2 obtained in the solid state are different from those obtained in solution.

(ii) The X-ray crystal structure determination has been crucial in identifying the I_7^- ion and both $[\mathbf{1}_2I]^+$ and $[\mathbf{2}_2I]^+$ cations; in particular, our I_7^- ion is the first to be described as $I^-{\cdot}3I_2$, and the cation $[\mathbf{2}_2I]^+$ is the first of this type with a Se donor.

(iii) Polyiodides having the same formula may exhibit a great variety of structures; as is well-known, the counterion plays an important role in determining its structure.

(iv) I_7^- ions may exhibit different Raman spectra, which are however well related to their structural features; this is also valid for the other polyiodides.

(v) Except for the symmetrical I_3^- case, the Raman technique is unable to distinguish each polyiodide and the polyiodides from the neutral adducts unambiguously, but it can give valuable information on the extent of the lengthening of the I–I bond, whether or not it has been produced by the interaction with a neutral donor or an ion.

Acknowledgment. This research was carried out as part of "Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate" of the "Consiglio Nazionale delle Ricerche". We thank Dr. R. Margarit of the Bruker Spectroscopin Italiana for his kindness in recording the FT-Raman spectra and Dr. P. Lukes of the Centre of Molecular Electronics of Durham (England) for his kindness in carrying out the conductivity measurements. We also thank one of the reviewers for a useful suggestion on the FT-Raman spectra discussion.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters and hydrogen atom locations (16 pages). Ordering information is given on any current masthead page.

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(42) In an idealized I_7^- ($I^-{\cdot}3I_2$) ion with a C_{3v} symmetry, the vibrations of the individual I_2 units combine to give normal modes of the A_1 + E type. The 175.2- and 157.4-cm^{-1} bands are likely to be the A_1 and E, respectively. The slight distortion of the symmetry from C_{3v} to C_s may redistribute the contribution of the individual I_2 groups: the shorter I_2 unit will give a greater contribution to the higher frequency band (A′ in C_s) and the longer I_2 units to the lower frequency band (E in C_{3v}, which splits in A′ + A″ in C_s). This symmetry lowering will mix the stretching modes with the effect of increasing the energy of the higher energy stretch and lowering the energy of the lower energy stretch. This view would explain the scatter from the correlation of the two frequencies (Figure 6).

(43) In this I_3^- ion, the I–I bond order (n), evaluated for the short I–I bond distance is 0.69, thus indicating that I_2 can be still considered a perturbed diatomic molecule.

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