Reaction of Bis(morpholinoselenocarbonyl) Triselenide with Iodine. Existence of a 1 : 1 Charge-transfer Precursory Adduct in Solution in an Oxidative Reaction. Isolation and Crystal Structure of the New (N-Morpholinecarbodiselenoato)selenium(II) iodide †

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The reaction of bis(morpholinoselenocarbonyl) triselenide, $Se_3[C(Se)NC_4H_8O]_2$ with iodine in CH_2Cl_2 has been investigated employing spectrophotometric measurements. Working with an excess of iodine, spectral features indicate the formation of a very stable 1 : 1 charge-transfer adduct. This species evolves [k_c = (10.1 ± 0.6) × 10^{-6} s^{-1} at 25 °C] and from the solution the new red-brown compound (morpholinecarbodiselenoato)selenium(II) iodide, $[OC_4H_8NCSe_3]I$, was isolated. Working with an excess of $Se_3[C(Se)NC_4H_8O]_2$ spectral results suggest the existence of an equilibrium between the 1 : 1 adduct and $Se_3[C(Se)NC_4H_8O]_2$, which yields products having a spectrum very similar to that of $[OC_4H_8NCSe_3]I$. The compound $[OC_4H_8NCSe_3]I$ was recovered also from the solutions of these mixtures. Crystals of the product are monoclinic, space group $P2_1/c$, with a = 8.62(5), b = 17.19(6), c = 14.59(6) Å, β = 101.1(1)°, and Z = 8. The structure consists of polymeric ··· I ··· Se ··· I ··· Se ··· I ··· chains running along c held together by van der Waals contacts.

It is well known that the carbonyl sulphur in thiones,[1] and better still the carbonyl selenium in selones,[2] form charge-transfer (c.t.) complexes with iodine. However, iodine also oxidizes thiuram disulphide co-ordinated to mercury in di-iodo(thiuram disulphide)mercury(II) giving a dipositive five-membered ring.[3]

We have recently observed that tris(morpholinecarbodithioato)- and tris(morpholinecarbodiselenoato)-cobalt(III) react with iodine to give a 1 : 1 c.t. adduct showing that, even if co-ordinated, sulphur and, more so, selenium atoms retain basic properties.[4]

Adduct formation may be mechanistically precursory in oxidative reactions. In order to help clarify the mechanism of the reactions of iodine with dithio- and diseleno-carbamato-derivatives, we here report a study on the reaction of iodine with bis(morpholinoselenocarbonyl) triselenide, $Se_3[C(Se)NC_4H_8O]_2$, in CH_2Cl_2, and also the crystal structure of the new compound (morpholinecarbodiselenoato)selenium(II) iodide, $[OC_4H_8NCSe_3]I$, obtained as crystals on long standing of the above solutions of the reagents.

Experimental

Materials.—Bisublimed iodine was purchased from Carlo Erba. Dichloromethane was Merck Reagent Grade and dried over 4A molecular sieves before use. Bis(morpholinoselenocarbonyl) triselenide was prepared and purified according to the literature method.[5]

Synthesis.—The compound $[OC_4H_8NCSe_3]I$ was obtained as red-brown lustrous crystals, on long standing of very dilute solutions of $Se_3[C(Se)NC_4H_8O]_2$ and iodine in a 1 : 1 ratio. The crystals are very slightly soluble in most solvents (Found: C, 12.8; H, 1.85; I, 26.25; N, 3.2. Calc. for $C_5H_8INOSe_3$: C, 13.0; H, 1.75; I, 27.5; N, 3.05%). The u.v.-visible spectrum is reported in Figure 1. I.r. (KBr pellets for the range 4 000—450 cm^{-1}, Nujol mulls on CsI discs for the range 450—200 cm^{-1}): 2 960 (sh), 2 920mw, 2 865mw, 1 528vs, 1 503mw, 1 458m, 1 418s, 1 410 (sh), 1 391w, 1 381w, 1 352ms, 1 300ms, 1 263s, 1 248vs, 1 105vs, 1 053m, 1 020vs, 872vs, 845ms, 805w, 663w, 635vs, 492s, 462m, 410m, 297m, and 245br cm^{-1}.

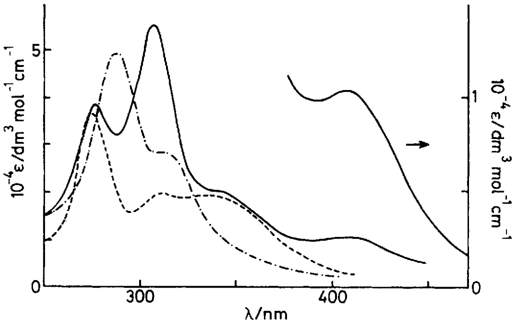

Figure 1. U.v.–visible spectra of $[OC_4H_8NCSe_3]I$ (— — —), $Se_3[C(Se)NC_4H_8O]_2$ (— · —), and $Se_3[C(Se)NC_4H_8O]_2 \cdot I_2$ (——)

Using different molar ratios it is possible to obtain the same product by working with an excess of $Se_3[C(Se)NC_4H_8O]_2$. Instead, using a large excess of iodine, we isolated a different dark red-brown solid. The analytical results agree with the formulation $[OC_4H_8NCSe_3]I_3$ (Found: C, 8.2; H, 1.1; N, 1.9. Calc. for $C_5H_8I_3NOSe_3$: C, 8.4; H, 1.15; N, 1.95%). I.r. (KBr pellets for the range 4 000—450 cm^{-1}, Nujol mulls on CsI discs for the range 450—200 cm^{-1}): 2 960 (sh), 2 920mw, 2 865mw, 1 545vs, 1 430m, 1 418m, 1 380m, 1 342m, 1 298m, 1 258ms, 1 242s, 1 110m, 1 098s, 1 055m, 1 018s, 863m, 630m, 496m, 410w, 328m, 282w, 268m, 253ms, and 230ms cm^{-1}.

The Elemental Analyses were performed by Istituto di Chimica Farmaceutica, University of Cagliari. The iodine

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† *Supplementary data available* (No. SUP 23604, 11 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

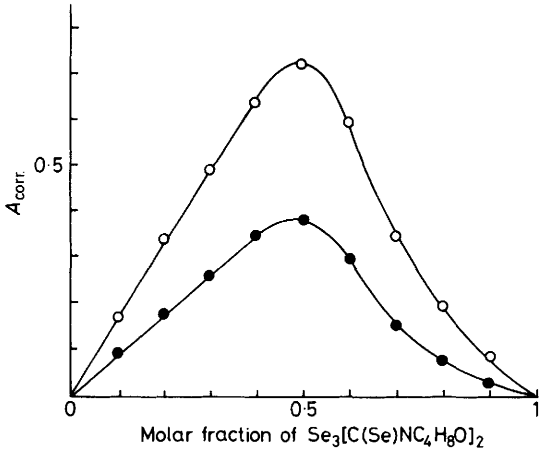

Figure 2. Job's plot for the system with $[Se_3\{C(Se)NC_4H_8O\}_2] + [I_2] = 2 \times 10^{-4}$ mol dm^{-3}, at 410 (○) and 440 nm (●)

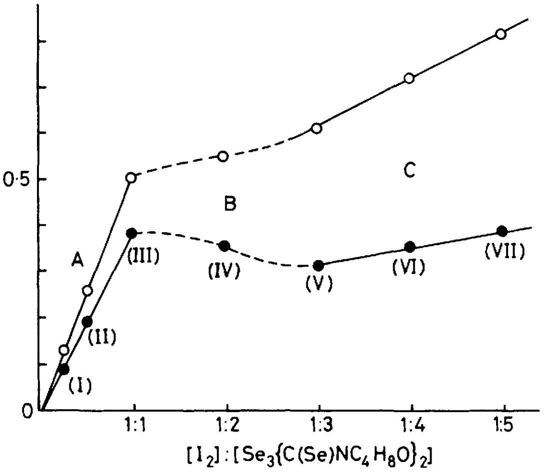

Figure 3. Molar ratio plot for the system $Se_3[C(Se)NC_4H_8O]_2 + I_2$, at 400 (○) and 430 nm (●)

was determined by a combustion method, followed by spectrophotometric determinations in CCl_4 of the sublimed iodine.

Apparatus.—U.v.–visible spectra were recorded on a Cary model 219 spectrophotometer, using 1-cm and 0.1-cm matched quartz cells, thermostatted at 25 ± 0.1 °C. Infrared spectra were recorded using a Perkin-Elmer model 325 spectrophotometer.

U.v.–Visible Spectra.—A fresh solution for each run was made up at 25 °C and stored in the dark throughout the whole experiment to avoid decomposition due to exposure to light. On long standing the reaction products showed a time dependence of the absorbance (see Results and Discussion section), therefore the absorbance values used to calculate the equilibrium constant were read immediately after mixing the reagents. At selected wavelengths for a series of 11 solutions having a total concentration of $[Se_3\{C(Se)NC_4H_8O\}_2] + [I_2] = 2 \times 10^{-4}$ mol dm^{-3} we obtained Job's plots by measuring the absorbances and subtracting those due to the free reagents (Figure 2).

The plot in Figure 3 was obtained by applying the molar ratio method using seven solutions with a constant iodine concentration of 5×10^{-5} mol dm^{-3} and $[Se_3\{C(Se)NC_4H_8O\}_2] = 1.25 \times 10^{-5}$ (I), 2.5×10^{-5} (II), 5×10^{-5} (III),10^{-4} (IV), 1.5×10^{-4} (V), 2.0×10^{-4} (VI), and 2.5×10^{-4} mol dm^{-3} (VII).

Kinetics.—The rate of $Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2$ adduct transformation was obtained at 25 °C by monitoring the absorbances of solution (III) ($[Se_3\{C(Se)NC_4H_8O\}_2]$: $[I_2]$ = 1 : 1) for about 100 h, at five different wavelengths (two examples are reported in Figure 4). The rate constant is calculated by applying the equation $\ln[(A_\infty - A_0)/(A_\infty - A_t)] = kt$ (where A_0, A_t, and A_∞ are the absorbance values at 0, t, and ∞ time respectively, at a given wavelength) and then averaging the five k values obtained.

X-Ray Crystal Structure Analysis.—*Crystal data.* $C_5H_8INOSe_3$,M = 461.909, Monoclinic, a = 8.62(5), b = 17.19(6), c = 14.59(6) Å, β = 101.1(1)°, U = 2 121(17) Å^3, Z = 8, D_c = 2.89 g cm^{-3}, $F(000)$ = 1 664, $\lambda(\text{Mo-}K_{\alpha 1})$ = 0.709 26 Å, $\mu(\text{Mo-}K_{\alpha 1})$ = 131.34 cm^{-1}, space group $P2_1/c$ (from structure determination).

A red crystal of the above compound having dimensions *ca.* 0.10 × 0.10 × 0.44 mm was mounted along a and used for the data collection. Preliminary cell parameters, obtained by rotation and Weissenberg photographs, were subsequently refined by least-squares methods from the θ values of 13 reflections accurately measured on a Siemens AED single-crystal diffractometer. A complete set of intensity data was collected within the angular range $2.5 \leqslant \theta \leqslant 25°$. The ω—2θ scan technique was used; a standard reflection was remeasured after every 50 reflections as a check on crystal and instrument stability (no significant change in the measured intensities of these reflections was observed during data collection). A total of 4 165 independent reflections were measured, of which 1 338 were considered observed and were employed in the analysis, having $I \geqslant 2\sigma(I)$. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. No correction was applied for absorption. The absolute scale and the mean temperature factor were established by Wilson's method.[6]

Structure determination and refinement. Initial co-ordinates of the heavy atoms were determined by a Patterson map. A Fourier synthesis, calculated with phases of these atoms, revealed the positions of all other non-hydrogen atoms. Refinement was carried out by full-matrix least-squares methods, using the SHELX system of computer programs,[7] first isotropically and then anisotropically. The difference electron-density map was not valuable in locating the hydrogen atoms. For the final refinement, seven reflections, 3 0 0, 4 0 0, 3 1 0, 6 1 1, 0 1 2, 7 1 3, and $\bar{4}$ 16 4, whose $|F_o|$ values indicated that they were affected by extinction or absorption when compared with their $|F_c|$ values, were omitted. The final R value was 0.035 (observed reflections only). The function minimized in the least-squares calculations was $\Sigma w|F^2|$ with $w = 0.2565/[\sigma^2(F_o) + 0.0064\ 15(F_o)^2]$. The atomic scattering factors used were taken from International Tables,[8] as were the real and imaginary parts of the anomalous scattering.[9] The final atomic co-ordinates with their estimated standard deviations are given in Table 1.

All calculations were performed on the CYBER 7600 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nordi-Orientale, Casalecchio (Bologna).

Results and Discussion

The addition of iodine to $Se_3[C(Se)NC_4H_8O]_2$ in CH_2Cl_2 is accompanied by a drastic change in the u.v.–visible spec-

Table 1. Final atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
I(1)	4 470(2)	1 219(1)	7 550(1)	N(2)	2 857(20)	−1 477(9)	4 709(10)
I(2)	641(2)	3 002(1)	9 067(1)	C(1)	−579(26)	100(11)	8 617(13)
Se(1)	1 212(3)	22(1)	8 084(1)	C(2)	−2 903(23)	−388(11)	9 181(13)
Se(2)	1 465(3)	1 386(1)	8 384(1)	C(3)	−4 313(28)	−794(13)	8 602(16)
Se(3)	−939(2)	1 104(1)	8 978(1)	C(4)	−2 690(28)	−1 630(12)	7 914(16)
Se(4)	3 771(3)	−361(1)	6 070(1)	C(5)	−1 222(30)	−1 276(11)	8 428(17)
Se(5)	2 687(3)	842(1)	5 477(1)	C(6)	2 760(22)	−762(11)	4 918(13)
Se(6)	1 641(2)	16(1)	4 195(1)	C(7)	1 745(29)	−1 772(12)	3 840(14)
O(1)	−3 971(18)	−1 583(9)	8 435(11)	C(8)	2 479(26)	−2 466(12)	3 456(14)
O(2)	2 849(19)	−3 023(7)	4 227(10)	C(9)	4 177(27)	−2 728(11)	4 920(14)
N(1)	−1 540(19)	−479(8)	8 717(10)	C(10)	3 664(27)	−2 031(12)	5 392(14)

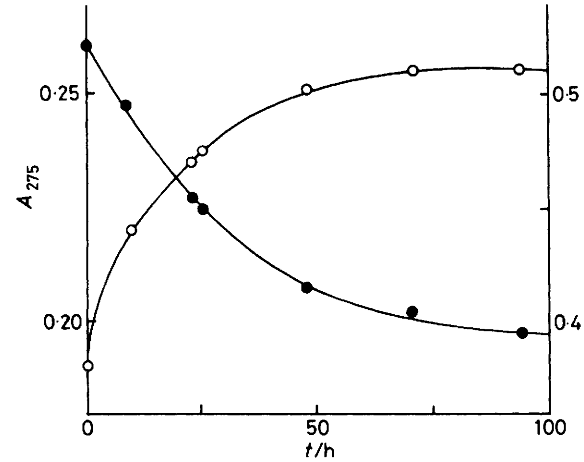

Figure 4. Absorbance of solution (III) ([$Se_3\{C(Se)NC_4H_8O\}_2$]: [I_2] = 1 : 1), at 275 (○) and 400 nm (●) against time

trum of the solution [see Figure 1]. Working with molar fractions of $Se_3[C(Se)NC_4H_8O]_2$ less than 0.5 a clear c.t. maximum is observed at 307 nm, while the characteristic bands of free $Se_3[C(Se)NC_4H_8O]_2$ and free iodine are ' blue-shifted '. In fact the band due to iodine at 520 nm is shifted to 410 nm and an isosbestic point is observed at 475 nm. Job's plots (Figure 2) at different wavelengths show a linear increase up to the point where the molar fraction 0.5 is reached, indicating that a stable c.t. 1 : 1 complex $Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2$ is formed. At higher molar fractions, however, these plots show an inflection which is not well resolved, that indicates a higher $Se_3[C(Se)NC_4H_8O]_2 : I_2$ reaction ratio.

By applying the molar ratio method {*i.e.* using constant [I_2] and increasing the concentration of $Se_3[C(Se)NC_4H_8O]_2$} the plot in Figure 3 is obtained. Three regions can be distinguished clearly: (*i*) the region A showing a linear increase of the absorbance up to the point where the exact 1 : 1 ratio is reached; (*ii*) the intermediate region B, that is characteristic of an equilibrium between the species $Se_3[C(Se)NC_4H_8O]{\cdot}I_2$ and another product whose formation is complete only in the linear region C; (*iii*) the region C that shows a linear increase of the absorbances which is due to the excess of $Se_3[C(Se)NC_4H_8O]_2$ alone (see below).

On this basis, working with a ratio of $I_2 : Se_3[C(Se)NC_4H_8O]_2$ of >1 : 1 the equilibrium (1) takes place in solution.

$$Se_3[C(Se)NC_4H_8O]_2 + I_2 \rightleftharpoons Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2 \quad (1)$$

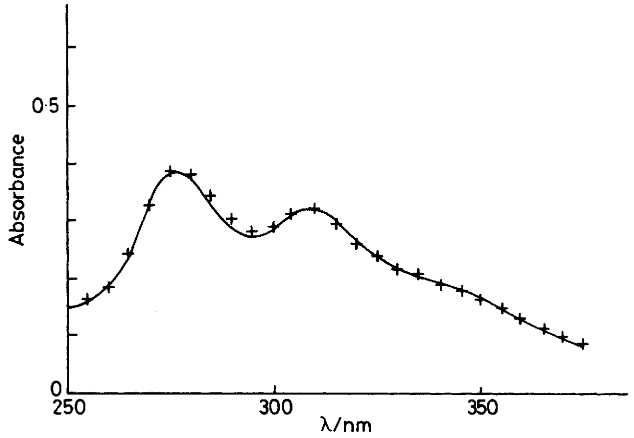

Figure 5. Experimental (——) and calculated (+) u.v.–visible spectra of solution (IV) (see Results and Discussion section)

The stability constant cannot be calculated, the saturation fraction in our experimental conditions being nearly 1, but it is expected to be $>10^6$ dm^3 mol^{-1}.[10] There is no evidence for any other stoicheiometry, even though $Se_3[C(Se)NC_4H_8O]_2$ contains multiple potentially active selenium sites.

A time dependence of the absorbance of the adduct $Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2$ is observed in Figure 4, equation (2). By plotting $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ *versus* time, a good

$$Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2 \xrightarrow{k_c} \text{products} \quad (2)$$

linear relationship is obtained, and the slope is $k_c = (10.1 \pm 0.6) \times 10^{-6}$ s^{-1}; $r = 0.99$ (r = correlation coefficient). Thus the reaction obeys first-order kinetics with respect to $Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2$.

On long standing (or better, using a more concentrated solution) a sparingly soluble red-brown solid crystallizes. *X*-Ray results (see below) have revealed that this solid is the new compound (morpholinecarbodiselenoato)selenium(II) iodide, $[OC_4H_8NCSe_3]I$.

The double-bond character of the CN linkage is reflected by the very high value of the ν(CN) stretch (1 528 cm^{-1}).[11] The u.v.–visible spectrum is reported in Figure 1.

The spectrum of the transformation products shows that they are made up of the species $[OC_4H_8NCSe_3]I$, together with an unidentified product which may be $OC_4H_8NCSe_2I$ (similar intermediate has been invoked in the corresponding sulphur derivative [12]) or its decomposition products.

Instead, in the presence of an excess of $Se_3[C(Se)NC_4H_8O]_2$ [solutions (IV)—(VII)] the reaction ratio is not obtained immediately from the plots of Figures 2 and 3. How-

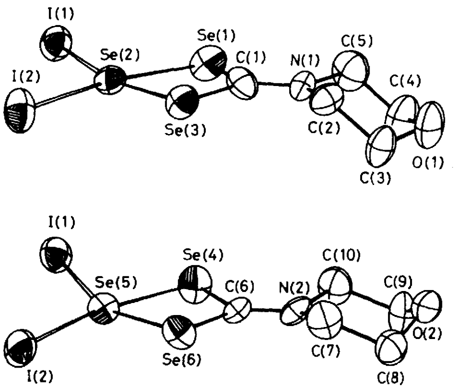

Figure 6. Perspective views of the two cations showing the co-ordination of the two independent selenium(II) atoms. In the lower perspective view I(2) is generated from the original one by a glide ($x, \frac{1}{2} - y, \frac{1}{2} + z$)

ever, using the hypothesis of a 3 : 2 stoicheiometry, reproducible equilibrium constants were obtained at any wavelength of the u.v. region, and by subtracting the contribution of the calculated excess of free $Se_3[C(Se)NC_4H_8O]_2$ in the region C of Figure 3 a spectrum very similar to that of $[OC_4H_8NCSe_3]I$ is always obtained.

Thus the reaction in the presence of an excess of $Se_3[C(Se)NC_4H_8O]_2$ may be expressed as in equation (3), where the

$$2\ Se_3[C(Se)NC_4H_8O]_2 + 2\ I_2 \overset{K^A}{\rightleftharpoons} 2\ Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2$$

$$2\ Se_3[C(Se)NC_4H_8O]_2{\cdot}I_2 + Se_3[C(Se)NC_4H_8O]_2 \overset{K_e}{\rightleftharpoons}$$
$$4\ [OC_4H_8NCSe_3]I + Se[C(Se)NC_4H_8O]_2 \quad (3)$$

bis(morpholinoselenocarbonyl) monoselenide [5] may be present for stoicheiometric reasons.

The presence of another species in addition to $[OC_4H_8NCSe_3]I$ in the final reaction products is indicated by the small discrepancies between the spectrum of pure $[OC_4H_8NCSe_3]I$ and that obtained by the above subtraction in the region C of Figure 3.

The evolution of the spectrum of these products with time may be ascribed to the transformation of the monoselenide to the triselenide and decomposition products. The equilibrium constant calculated on this basis is $K_e = (3.8 \pm 0.5) \times 10^{-8}$ mol^2 dm^{-6} at 25 °C, and by using this K_e value and the ε values of the reagents and the products, a very good fitting of the experimental spectra is obtained, as reported for solution (IV) in Figure 5.

On long standing, the compound $[OC_4H_8NCSe_3]I$ also crystallizes from solutions (IV)—(VII), while the mother-liquor contains principally $Se_3[C(Se)NC_4H_8O]_2$.

Crystal and Molecular Structure.—Figure 6 shows the structures with the atom-numbering schemes of the two crystallographically independent (morpholinecarbodiselenoato)selenium(II) cations and their interactions with the two iodide ions. Bond distances and angles involving all the non-hydrogen atoms are given in Table 2. The co-ordination of each central Se atom belongs to 'class II' according to Bröndmo *et al.*[13] In fact, in the resulting $SeSe_2I_2$ groups, each central atom is more strongly bonded to the two Se atoms of the bidentate ligand than to the two iodine ions. A similar class was observed in selenium bis(diethyldiselenophosphinate) [14] and in tellurium bis(diethylthioselenophosphinate) [15] where, however, no chelated ring is observed.

The co-ordination around each central Se atom is trapezoidal and strictly planar only around Se(1) (Table 3). The angle between the trapezium bases Se(1)–Se(3) and I(1)–I(2) is 1.9(3)° and that between Se(4)–Se(6) and I(1)–I(2) ($x, \frac{1}{2} - y, \frac{1}{2} + z$) is 1.8(3)°. The stronger central atom-to-ligand bonds Se(2)–Se(1), Se(2)–Se(3) and Se(5)–Se(4), Se(5)–Se(6) are 2.39(1), 2.44(1) and 2.36(1), 2.38(1) Å respectively for both molecules. These bond distances lie in the range 2.315—2.479 Å observed in the complexes of selenium(II) with diselenocarbamate [16,17] and diselenophosphinate [14] ligands, in di-, tri-, and tetra-selane,[18,19] in the allotropic forms of selenium,[20-22] in selenium diselenocyanate,[23] and in 1*H*,4*H*-naphtho[1.8]-disenepine.[24,*]

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

I(1)–Se(2)	3.08(1)	I(2)–Se(2)	3.08(1)
I(1)–Se(5)	3.18(1)	I(2)–Se(5^{II})	3.15(1)
Se(1)–Se(2)	2.39(1)	Se(4)–Se(5)	2.36(1)
Se(2)–Se(3)	2.44(1)	Se(5)–Se(6)	2.38(1)
Se(1)–C(1)	1.86(2)	Se(4)–C(6)	1.87(2)
Se(3)–C(1)	1.85(2)	Se(6)–C(6)	1.85(2)
C(1)–N(1)	1.32(3)	C(6)–N(2)	1.27(2)
N(1)–C(2)	1.47(3)	N(2)–C(7)	1.52(2)
C(2)–C(3)	1.51(3)	C(7)–C(8)	1.51(3)
C(3)–O(1)	1.42(3)	C(8)–O(2)	1.46(2)
O(1)–C(4)	1.46(3)	O(2)–C(9)	1.46(2)
C(4)–C(5)	1.47(3)	C(9)–C(10)	1.49(3)
C(5)–N(1)	1.47(3)	C(10)–N(2)	1.46(2)

Se(2)–I(1)–Se(5)	96.1(5)	Se(2)–I(2)–Se(5^{II})	130.3(5)
Se(1)–Se(2)–I(1)	83.7(5)	Se(4)–Se(5)–I(1)	75.3(5)
Se(1)–Se(2)–I(2)	157.9(5)	Se(4)–Se(5)–I(2^{I})	157.6(5)
Se(1)–Se(2)–Se(3)	79.4(5)	Se(4)–Se(5)–Se(6)	80.2(5)
I(1)–Se(2)–I(2)	118.4(5)	I(1)–Se(5)–I(2^{I})	126.9(5)
I(1)–Se(2)–Se(3)	163.1(5)	I(1)–Se(5)–Se(6)	155.1(5)
I(2)–Se(2)–Se(3)	78.5(5)	I(2^{I})–Se(5)–Se(6)	77.5(5)
Se(2)–Se(1)–C(1)	84.6(8)	Se(5)–Se(4)–C(6)	84.9(8)
Se(2)–Se(3)–C(1)	83.3(9)	Se(5)–Se(6)–C(6)	84.6(9)
Se(1)–C(1)–Se(3)	112.6(14)	Se(4)–C(6)–Se(6)	110.3(12)
Se(1)–C(1)–N(1)	125.4(17)	Se(4)–C(6)–N(2)	122.0(18)
Se(3)–C(1)–N(1)	121.9(18)	Se(6)–C(6)–N(2)	127.7(18)
C(1)–N(1)–C(2)	122.9(18)	C(6)–N(2)–C(7)	117.5(19)
C(1)–N(1)–C(5)	120.9(21)	C(6)–N(2)–C(10)	120.8(19)
C(2)–N(1)–C(5)	116.0(18)	C(7)–N(2)–C(10)	119.6(18)
N(1)–C(2)–C(3)	108.7(19)	N(2)–C(7)–C(8)	109.3(20)
C(2)–C(3)–O(1)	111.5(20)	C(7)–C(8)–O(2)	106.1(18)
C(3)–O(1)–C(4)	110.2(19)	C(8)–O(2)–C(9)	109.2(17)
O(1)–C(4)–C(5)	112.0(21)	O(2)–C(9)–C(10)	109.6(20)
C(4)–C(5)–N(1)	109.9(20)	C(9)–C(10)–N(2)	110.8(19)

Key to symmetry operations: I $x, \frac{1}{2} - y, -\frac{1}{2} + z$; II, $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The longer bonds Se(2)–I(1), Se(2)–I(2), Se(5)–I(1), and Se(5)–I(2) ($x, \frac{1}{2} - y, \frac{1}{2} + z$), which are *trans* to the strong ones, are 3.08(1), 3.08(1), 3.18(1), and 3.15(1) Å, respectively. These interactions, longer than those observed in the adducts of iodine with 1-oxa-4-selenacyclohexane [25] [2.755(4) Å], with tetrahydroselenophene [26] [2.762(5) Å], with 1,4-diselenane [27] [2.829(4) Å], and in the iodine monochloride complex of 1-oxa-4-selenacyclohexane [28] [2.630(5) Å], determine polymeric chains of the type $\cdots$ I(1) $\cdots$ Se(2) $\cdots$ I(2) $\cdots$ Se(5) $\cdots$ I(1) $\cdots$ (Figure 7).

Both morpholine rings adopt a slightly distorted chair conformation, as indicated by the torsion angles, by the ring-puckering parameters [29] for sequences O(1),C(3),C(2),N(1), C(5),C(4) and O(2),C(8),C(7),N(2),C(10),C(9) and by the asymmetry parameters [30] (Table 4). In addition, all these parameters prove a greater distortion in the second ring.

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[*] 7*H*, 10*H*, 17*H*, 20*H*—Dinaphtho[1,8-*de*; 1′,8′-*kl*][1,2,8,9]tetraselenacyclotetradecine.

Table 3. Weighted least-squares planes [a] and lines [b] with deviations (Å) and e.s.d.s of the relevant atoms in square brackets

Plane	*A*	*B*	*C*	*D*	Deviations
Plane 1: Se(1), Se(3), I(1), I(2), Se(2)	−0.373 32	0.192 56	−0.907 50	−10.043 15	[Se(1) +0.00(1), Se(3) −0.01(1), I(1) −0.01(1), I(2) +0.00(1), Se(2) +0.02(1), C(1) −0.03(2), N(1) −0.03(2)]
Plane 2: Se(1), Se(3), I(1), I(2)	−0.373 17	0.192 69	−0.907 53	−10.047 57	[Se(1) +0.01(1), Se(3) −0.01(1), I(1) −0.01(1), I(2) +0.01(1), Se(2) +0.02(1), C(1) −0.03(2), N(1) −0.03(2)]
Plane 3: Se(4), Se(6), I(1), I(2$^{\text{I}}$), Se(5)	0.904 73	0.210 06	−0.370 60	−1.965 49	[Se(4) +0.01(1), Se(6) −0.04(1), I(1) −0.03(1), I(2$^{\text{I}}$) −0.00(1), Se(5) +0.07(1), C(6) −0.02(2), N(2) −0.03(2)]
Plane 4: Se(4), Se(6), I(1), I(2$^{\text{I}}$)	0.904 59	0.211 23	−0.370 28	−1.978 17	[Se(4) +0.03(1), Se(6) −0.03(1), I(1) −0.01(1), I(2$^{\text{I}}$) +0.01(1), Se(5) +0.08(1), C(6) −0.00(2), N(2) −0.02(2)]
Plane 5: N(1), C(1), Se(1), Se(2), Se(3), C(2), C(5)	−0.390 51	0.183 88	−0.902 05	−9.955 19	[N(1) +0.02(2), C(1) −0.00(2), Se(1) +0.00(1), Se(2) −0.01(1), Se(3) +0.01(1), C(2) −0.04(2), C(5) +0.00(3), C(3) +0.99(3), C(4) +0.99(3), O(1) +0.82(2), I(1) −0.09(1), I(2) −0.03(1)]
Plane 6: N(2), C(6), Se(4), Se(5), Se(6), C(7), C(10)	0.898 63	0.169 68	−0.404 56	−2.220 39	[N(2) +0.09(2), C(6) +0.05(2), Se(4) −0.01(1), Se(5) −0.01(1), Se(6) +0.01(1), C(7) −0.14(3), C(10) −0.02(3), C(9) +0.57(3), C(8) +0.55(3), O(2) +0.03(2), I(1) −0.24(1), I(2$^{\text{I}}$) −0.08(1)]
Plane 7: Se(1), Se(2) Se(3), C(1), N(1)	−0.384 67	0.186 66	−0.903 98	−9.985 46	[Se(1) +0.00(1), Se(2) −0.00(1), Se(3) +0.00(1), C(1) −0.01(2), N(1) +0.00(2), C(2) −0.07(2), C(5) −0.02(3), C(3) +0.96(3), C(4) +0.97(3), O(1) +0.79(2), I(1) −0.06(1), I(2) −0.02(1)]
Plane 8: Se(4), Se(5), Se(6), C(6), N(2)	0.899 88	0.186 81	−0.394 12	−2.135 35	[Se(4) −0.01, Se(5) +0.02(1), Se(6) −0 01(1), C(6) +0.01(2), N(2) +0.03(2), C(10) −0.08(3), C(7) −0.22(3), C(9) +0.48(3), C(8) +0.44(3), O(2) −0.08(2), I(1) −0.17(1), I(2$^{\text{I}}$) −0.05(1)]
Plane 9: C(1), C(2), C(5)	0.407 00	−0.188 48	0.893 77	9.805 80	[C(1) +0.00(2), C(2) +0.00(2), C(5) +0.00(3), N(1) −0.03(2)]
Plane 10: C(6), C(7), C(10)	−0.880 51	−0.117 97	0.459 11	2.508 70	[C(6) +0.00(2), C(7) +0.00(3), C(10) +0.00(3), N(2) −0.12(2)]

	X_0	Y_0	Z_0
Line 1: Se(1)Se(3)	−2.278 61	0.967 80	12.213 88
Line 2: I(1)I(2)	−0.130 93	3.627 95	11.895 33
Line 3: Se(4)Se(6)	0.890 91	−0.296 53	7.348 23
Line 4: I(1)I(2$^{\text{I}}$)	0.571 29	2.765 01	8.316 06

	M_1	M_2	M_3
Line 1: Se(1)Se(3)	−0.681 97	0.602 50	0.414 62
Line 2: I(1)I(2)	−0.704 29	0.579 23	0.410 45
Line 3: Se(4)Se(6)	−0.428 43	0.212 04	−0.878 34
Line 4: I(1)I(2$^{\text{I}}$)	−0.410 18	0.236 53	−0.880 80

[a] The equations are in the form $AX + BY + CZ = D$, where X, Y, Z are orthogonal co-ordinates (in Å) measured along a, b, c^*. [b] The equations are in the form $(X - X_0)/M_1 = (Y - Y_0)/M_2 = Z - Z_0/M_3$, where M_1, M_2, M_3 are the direction cosines referred to the X, Y, Z orthogonal axes; X_0, Y_0, Z_0 are the co-ordinates of the centroid of the set of atoms.

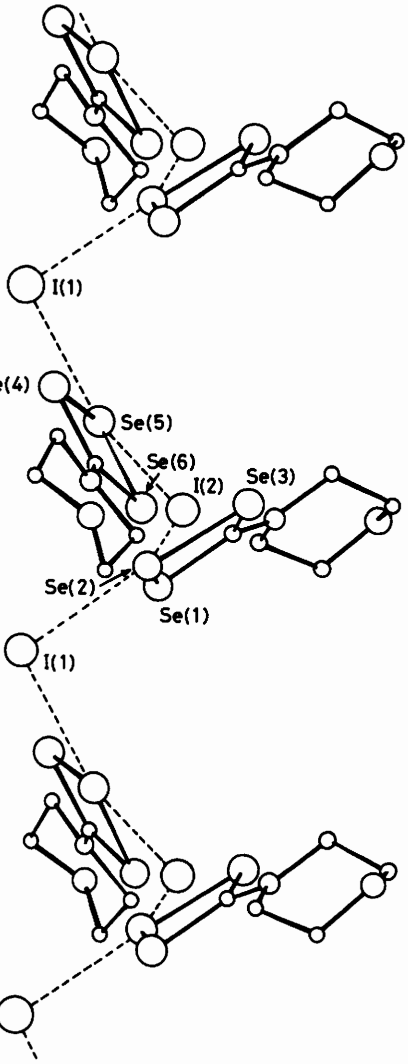

Figure 7. Polymeric chain viewed along [010]

The angles Se−Se−Se [79.4(5) and 80.2(5)°] are greater than those observed in bis(*NN*-diethyldiselenocarbamato)selenium(II)[16] (73.5—74.3°) and in selenium bis(1-pyrrolidinecarbodiselenoate)[17] [73.72(3)—73.84(3)°], containing similar chelate rings, which, however, belong to the ' class I '.

The angles around C(1) and C(6) indicate a sp^2 hybridization of these atoms. Although the statistical sginificance test indicates that all bond lengths and bond angles probably do not differ in both cations, it seems to us reasonable to assume that the differences are significant as can be assessed by the analysis of the planarities: N(1) is only 0.03 Å out of the C(1),C(2),C(5) plane whereas N(2) is 0.12 Å out of the C(6),C(7),C(10) plane (Table 3). These different displacements imply the greatest differences in the torsion angles (τ) between the two cations {τ[C(1)−N(1)−C(2)−C(3)] = 135(2), τ[C(1)−N(1)−C(5)−C(4)] = −136(2), τ[C(6)−N(2)−C(7)−C(8)] = 154(2), τ[C(6)-N(2)−C(10)−C(9)] = −158(2)°}. The C_2NCSe_3 fragment (above) is perfectly planar in the first cation, the deviations from the

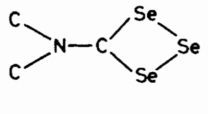

Table 4. Conformational analysis of the ' morpholinium ' cations

(*a*) Torsion angles (°)

	Ring 1
τ[C(5)–N(1)–C(2)–C(3)]	−49(3)
τ[N(1)–C(2)–C(3)–O(1)]	55(3)
τ[C(4)–O(1)–C(3)–C(2)]	−61(3)
τ[C(3)–O(1)–C(4)–C(5)]	61(3)
τ[O(1)–C(4)–C(5)–N(1)]	−53(3)
τ[C(2)–N(1)–C(5)–C(4)]	49(3)

	Ring 2
τ[C(10)–N(2)–C(7)–C(8)]	−42(3)
τ[N(2)–C(7)–C(8)–O(2)]	55(2)
τ[C(9)–O(2)–C(8)–C(7)]	−71(2)
τ[C(8)–O(2)–C(9)–C(10)]	69(2)
τ[O(2)–C(9)–C(10)–N(2)]	−49(3)
τ[C(7)–N(2)–C(10)–C(9)]	39(3)

(*b*) Ring-puckering parameters

q_2	0.08 Å	q_2	0.21 Å
φ_2	11°	φ_2	13°
q_3	0.53 Å	q_3	0.54 Å
Q	0.54 Å	Q	0.58 Å
θ_2	8°	θ_2	21°

(*c*) Asymmetry parameters (°)

ΔC_s[C(3)]	8	ΔC_s[C(8)]	19
ΔC_s[O(1)]	1	ΔC_s[O(2)]	4
ΔC_s[C(2)]	9	ΔC_s[C(7)]	23
ΔC_2[C(2)–C(3)]	12	ΔC_2[C(7)–C(8)]	30
ΔC_2[N(1)–C(2)]	7	ΔC_2[N(2)–C(7)]	19
ΔC_2[N(1)–C(5)]	5	ΔC_2[N(2)–C(10)]	11

weighted least-squares plane being greater in the second (Table 3).

The structure (Figure 8) consists of polymeric chains running along *c* held together by van der Waals contacts of the type Se(1) ··· Se(6) $(-x, -y, 1 - z)$ = 3.74(1) Å, I(1) ··· Se(3) $(1 + x, y, z)$ = 4.11(1) Å, and C(9) ··· O(1) $(1 + x, -\frac{1}{2} - y, -\frac{1}{2} + z)$ = 3.16(3) Å.

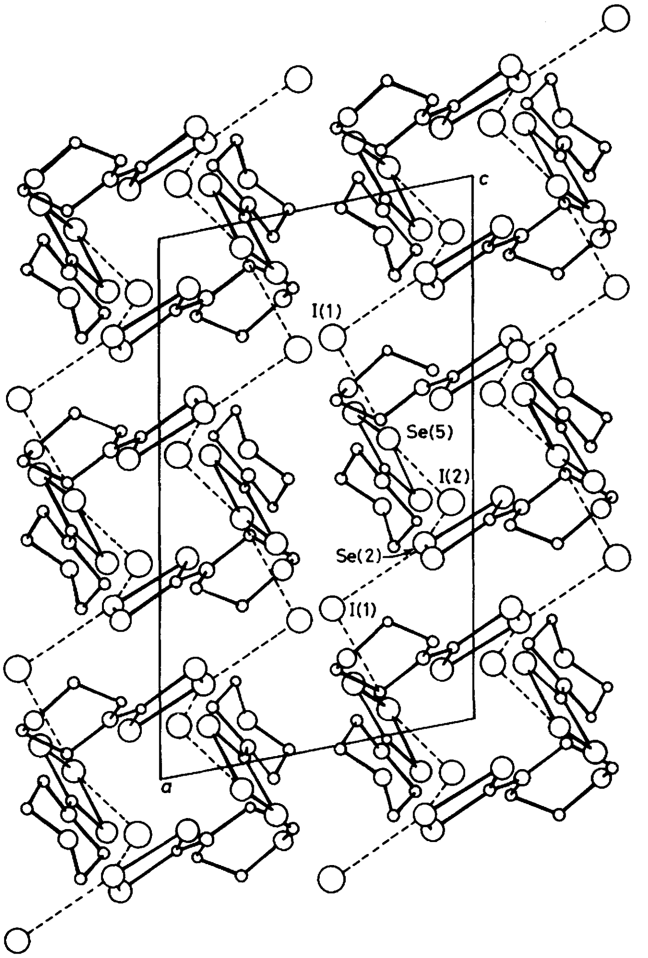

Figure 8. Projection of the structure along [010]

Conclusions

The results obtained demonstrate that c.t. adduct formation precedes the oxidation of $Se_3[C(Se)NC_4H_8O]_2$ by iodine. Generally, sulphur and selenium derivatives show similar behaviour[31] in their corresponding compounds, and a comparison of the above results with those previously reported on thiones having multiple sulphur sites allows us to observe the following. (*i*) As with the sulphur derivatives, $Se_3[C(Se)NC_4H_8O]_2$ and iodine interact to form a c.t. adduct in 1 : 1 ratio, even though the molecules have several electron donor sites. This may be explained by admitting that the donation of electrons from one S or Se atom produces a strong electron-withdrawing effect from the molecules, lowering the basicity of the other active sites. (*ii*) The compound $Se_3[C(Se)NC_4H_8O]_2$ gives a more stable adduct [*e.g.* note the much higher blue shift and stability constant with respect to those of bis(diethylthiocarbamoyl) disulphide, $\lambda_{max.}$ = 460 nm and k = 175 dm^3 mol^{-1}].[1] (*iii*) The isolated compound $[OC_4H_8NCSe_3]I$, with a monopositive cation, has no corresponding sulphur derivative.

The observed differences of the two classes of compounds may be accounted for by considering the greater polarizability and lower ionization potential of the selenium atom compared with sulphur.[32]

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