# Solid state structure and solution behaviour of organoselenium(II) compounds containing $2-\{E(CH_2CH_2)_2NCH_2\}C_6H_4$ groups (E = O, NMe)<sup>†</sup>

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Cleavage of the Se–Se bond in  $[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]_2Se_2$  (1) and  $[2-{MeN(CH_2CH_2)_2NCH_2}-C_6H_4]_2Se_2$  (2) by treatment with SO<sub>2</sub>Cl<sub>2</sub>, bromine or iodine (1 : 1 molar ratio) yielded  $[2-{O(CH_2CH_2)_2NCH_2}-NCH_2]C_6H_4]SeX$  [X = Cl (3), Br (4), I (5)] and  $[2-{MeN(CH_2CH_2)_2NCH_2}C_6H_4]SeI$  (6). The compounds were characterized in solution by NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, <sup>77</sup>Se, 2D experiments). The solid-state molecular structures of 1–3, 4·HBr, 5 and 6 were established by single crystal X-ray diffraction. In all cases T-shaped coordination geometries, *i.e.* (*C*,*N*)SeSe (1, 2), (*C*,*N*)SeX (3, 5, 6; X = halogen) or CSeBr<sub>2</sub> (4·HBr), were found. Supramolecular associations in crystals based on hydrogen contacts are discussed.

# Introduction

The chemistry of organoselenium(II) compounds containing an intramolecular  $N \rightarrow Se$  interaction has attracted considerable interest in recent years,<sup>1-5</sup> mainly due to their use in organic synthesis, as enzyme mimics and chemotherapeutic agents or the potential of 2-(*N*,*N*-dimethylaminomethyl)phenyl and related derivatives to stabilize exotic species such as the covalent azide [2-(Me<sub>2</sub>NCH<sub>2</sub>)-C<sub>6</sub>H<sub>4</sub>]SeN<sub>3</sub>,<sup>5</sup> or the trihalide [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]SeCl<sub>3</sub>.<sup>6</sup> Recently, we have reported on the synthesis, solution behaviour and molecular structures of various hypervalent organoselenium compounds containing the 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> group.<sup>6,7</sup> As a development of our previous studies on organoselenium compounds we decided to use bulkier organic groups with potential for additional coordination to the chalcogen centre through donor atoms.

We report here on the synthesis and characterization, both in solution and solid state, of new hypervalent organoselenium compounds containing  $2-\{E(CH_2CH_2)_2NCH_2\}C_6H_4$  moieties (E = O, NMe).

# **Results and discussion**

#### Synthesis

The new diorganodichalcogen(I) derivatives  $[2-{O(CH_2CH_2)_2-NCH_2}C_6H_4]_2Se_2$  (1) and  $[2-{MeN(CH_2CH_2)_2NCH_2}C_6H_4]_2Se_2$ 

(2) were obtained using the *ortho*-lithiation route.<sup>8</sup> The organolithium reagents  $[2-E(CH_2CH_2)_2NCH_2]C_6H_4]Li$  (E = O, NMe) were obtained as white solids by the direct metallation of 2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4Br$  with *n*-BuLi in anhydrous hexanediethyl ether. The treatment of a THF solution of RLi with finely ground selenium powder, under argon, followed by air oxidation, resulted in isolation of R–Se–Se–R derivatives (Scheme 1).

$$RBr \xrightarrow{+BuLi} RLi \xrightarrow{+Se} RSeLi \xrightarrow{+O_2 / H_2O} R_2Se_2$$

$$RBr \xrightarrow{+BuLi} RLi \xrightarrow{+Se} RSeLi \xrightarrow{+O_2 / H_2O} R_2Se_2$$

$$1, 2$$

$$X_2 (1:1) \xrightarrow{-SO_2} 2 RSeCl$$

$$X_2 (1:1) \xrightarrow{-SO_2} 2 RSeCl$$

$$X_2 (1:1) \xrightarrow{-SO_2} 2 RSeCl$$

$$4 - 6$$

$$R = 2 \cdot [E(CH_2CH_2)_2NCH_2]C_6H_4$$

$$X = - Cl Br l$$

$$E = O \quad 1 \quad 3 \quad 4 \quad 5$$

$$E = NMe \quad 2 \quad - \quad -6$$
Scheme 1

The organoselenium(II) halides,  $[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]$ -SeX [X = Cl (3), Br (4), I (5)] and  $[2-{MeN(CH_2CH_2)_2NCH_2}-C_6H_4]$ SeI (6), were prepared in good yield by cleavage of the Se–Se bond with SO<sub>2</sub>Cl<sub>2</sub>, elemental Br<sub>2</sub> or I<sub>2</sub> (1 : 1 molar ratio), respectively, at room temperature, in carbon tetrachloride or chloroform (Scheme 1).

The compounds were isolated as stable, yellow (1-4) or red (5, 6) crystalline solids from  $CH_2Cl_2$ -n-hexane mixtures. Elemental analytical data, together with NMR data are consistent with the anticipated formulas. Single crystals suitable for X-ray diffraction studies were obtained from a  $CH_2Cl_2$ -n-hexane mixture for all compounds.

#### Solid state and solution behavior

In order to reveal the extent to which the nitrogen atom of the 2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4$ - group is coordinated to the selenium center and the changes induced by the nature of the halogen atoms, the molecular structures of compounds 1–3, 4·HBr, 5 and 6 were determinated by single-crystal X-ray diffraction.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Figures representing the supramolecular architectures in the crystals of compounds **2**, **3**, **4**·HBr, **5** and **6**; simulation of the aliphatic region of <sup>1</sup>H NMR spectrum of **3**; variable temperature NMR data for **5**; selected <sup>15</sup>N and <sup>77</sup>Se NMR spectra. See DOI: 10.1039/b702629c

Table 1 Selected bond distances (Å) and angles (°) for compounds 1 and 2

1				2			
Se(1)–Se(2)	2.3458(5)			Se(1)-Se(2)	2.3700(5)		
Se(1) - C(1)	1.940(4)	Se(2)-C(12)	1.934(3)	Se(1) - C(1)	1.929(3)	Se(2) - C(13)	1.937(3)
Se(1) - N(1)	2.813(2)	Se(2)-N(2)	2.825(3)	Se(1)-N(1)	3.135(3)	Se(2)-N(3)	2.739(3)
N(1)-C(7)	1.434(5)	N(2) - C(18)	1.448(5)	N(1)-C(7)	1.453(5)	N(3) - C(19)	1.469(5)
N(1)-C(8)	1.444(5)	N(2) - C(19)	1.450(4)	N(1)-C(8)	1.445(5)	N(3) - C(20)	1.450(5)
N(1)-C(11)	1.452(5)	N(2) - C(22)	1.451(4)	N(1)-C(11)	1.471(4)	N(3) - C(23)	1.452(4)
O(1) - C(9)	1.418(5)	O(2) - C(20)	1.390(5)	N(2)–C(9)	1.450(5)	N(4) - C(21)	1.451(5)
O(1) - C(10)	1.402(5)	O(2) - C(21)	1.417(5)	N(2)-C(10)	1.440(5)	N(4) - C(22)	1.444(5)
				N(2)-C(12)	1.451(5)	N(4) - C(24)	1.458(5)
C(1)-Se(1)-Se(2)	104.30(11)	C(12)-Se(2)-Se(1)	104.45(10)	C(1)-Se(1)-Se(2)	100.34(10)	C(13)-Se(2)-Se(1)	101.13(11)
N(1)-Se(1)-C(1)	74.95(12)	N(2)-Se(2)-C(12)	74.55(12)	N(1)-Se(1)-C(1)	71.05(11)	N(3)-Se(2)-C(13)	74.81(12)
N(1)-Se(1)-Se(2)	162.65(6)	N(2)-Se(2)-Se(1)	166.39(5)	N(1)-Se(1)-Se(2)	165.33(6)	N(3)-Se(2)-Se(1)	171.89(7)
Se(1)-N(1)-C(7)	89.2(2)	Se(2)-N(2)-C(18)	86.6(2)	Se(1)-N(1)-C(7)	75.1(2)	Se(2)-N(3)-C(19)	88.9(2)
Se(1)-N(1)-C(8)	112.6(2)	Se(2)-N(2)-C(19)	112.0(2)	Se(1)-N(1)-C(8)	127.6(2)	Se(2)-N(3)-C(20)	109.8(2)
Se(1)-N(1)-C(11)	118.3(2)	Se(2)-N(2)-C(22)	121.7(2)	Se(1)-N(1)-C(11)	116.7(2)	Se(2)-N(3)-C(23)	120.5(2)
C(7)-N(1)-C(8)	112.7(3)	C(18)–N(2)–C(19)	113.2(3)	C(7)-N(1)-C(8)	111.6(3)	C(19)-N(3)-C(20)	112.4(3)
C(7)-N(1)-C(11)	113.2(3)	C(18)–N(2)–C(22)	112.5(3)	C(7)-N(1)-C(11)	110.2(3)	C(19)–N(3)–C(23)	112.6(3)
C(8)–N(1)–C(11)	109.6(3)	C(19)–N(2)–C(22)	109.2(3)	C(8)–N(1)–C(11)	109.2(3)	C(20)–N(3)–C(23)	110.9(3)
C(9)–O(1)–C(10)	108.9(3)	C(20)–O(2)–C(21)	110.2(3)	C(9)–N(2)–C(10)	109.1(3)	C(21)-N(4)-C(22)	108.8(3)
				C(9) - N(2) - C(12)	111.0(3)	C(21)-N(4)-C(24)	111.4(4)
				C(10) - N(2) - C(12)	112.7(4)	C(22)–N(4)–C(24)	110.6(3)

The molecular structures of the diselenides 1 and 2 are shown in Fig. 1 and 2 and the selected interatomic distances and angles are listed in Table 1. In both compounds intramolecular selenium-nitrogen interactions of significant strength are established, *i.e.* Se(1)...N(1) 2.813(2) Å, Se(2)...N(2) 2.825(3) Å for 1, and Se(1)...N(1) 3.135(3) Å, Se(2)...N(3) 2.739(3) Å for 2 [cf. the sums of the covalent radii,  $\sum r_{cov}(Se,N)$  1.87 Å, and of the corresponding van der Waals radii for selenium and nitrogen,  $\sum r_{vdW}$  (Se,N) 3.54 Å].<sup>9</sup> These interatomic distances are comparable with those observed in other related derivatives, e.g. [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se<sub>2</sub> [2.856(3), 2.863(4) Å],<sup>8</sup> bis[2-(4,4dimethyl-2-oxazolinyl)phenyl]diselenide [2.819(5), 2.705(5) Å].<sup>10,11</sup> The strong asymmetry of the Se-N bond lengths as observed for 2 was suggested to be the result of steric effects.<sup>11</sup> As a result of the intramolecular  $N \cdots Se$  interaction the coordination geometry around the selenium atoms is distorted T-shaped



Fig. 1 ORTEP representation at 30% probability and atom numbering scheme for the  $(R_{N1}, S_{N2})$ -1 isomer.



**Fig. 2** ORTEP representation at 30% probability and atom numbering scheme for the  $(R_{N1}, S_{N3})$ -2 isomer. Hydrogen atoms are omitted.

[(C,N)SeSe core, hypervalent 10-Se-3 species<sup>12</sup>], with the vector of the Se  $\cdots$  N interaction directed almost *trans* to the Se–Se bond  $[N(1) \cdots Se(1)-Se(2) \ 162.65(6)^{\circ}, \ N(2) \cdots Se(2)-Se(1) \ 166.39(5)^{\circ}$ for **1**, and N(1)  $\cdots$  Se(1)–Se(2)  $165.33(6)^{\circ}, \ N(3) \cdots Se(2)$ –Se(1) 171.89(7)° for **2**]. The coordination geometry around the Se atoms can be alternatively described as *pseudo*-trigonal bipyramidal, with N and the second Se atoms in axial positions and two lone pairs and the carbon atom in the equatorial plane.

The Se(1)–Se(2) distance in 1 [2.3458(5) Å] and 2 [2.3700(5) Å] is somewhat longer than those observed in other  $R_2Se_2$  derivatives [2.29–2.39 Å].<sup>11</sup> They are close to the Se–Se bond distances reported for related compounds [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se<sub>2</sub> [2.357(1) Å],<sup>8</sup> and bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl]-diselenide [2.354(8) Å].<sup>10,11</sup>

The conformation of the C–Se–Se–C skeleton can be discussed in terms of "cisoid" (C–Se–Se–C torsion angle smaller than  $90^{\circ}$ ) and "transoid" conformations (C–Se–Se–C torsion angle larger than  $90^{\circ}$ ). The C–Se–Se–C torsion angle is  $80.9^{\circ}$  in 1 and  $114.0^{\circ}$ 

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in **2**, thus consistent with a "cisoid" and a "transoid" arrangement, respectively. The morpholinyl and piperazinyl rings exhibit a *chair* conformation which prevents further intramolecular coordination to the selenium centers.

The intramolecular coordination of the nitrogen from the pendant arm to the selenium atom results in a five-membered SeC<sub>3</sub>N ring. The ring is not planar but folded along the Se(1)  $\cdots$  C<sub>methylene</sub> axis, with the nitrogen atom lying out of the best plane defined by the residual SeC<sub>3</sub> system. This induces planar chirality [with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively]<sup>13</sup> as described for other related compounds.<sup>6,14-18</sup> Indeed, the diselenides reported here crystallize as racemates, *i.e.* 1 : 1 mixtures of ( $R_{N1}$ , $S_{N2}$ ) and ( $S_{N1}$ , $R_{N2}$ ) 1 and ( $R_{N1}$ , $S_{N3}$ ) and ( $S_{N1}$ , $R_{N3}$ ) isomers for 2 (with respect to the two chelate rings in a molecular unit).

While discrete molecules of the disclenide 1 are present in the crystal (no contacts shorter than the sum of the van der Waals radii between heavy atoms, or a heavy atom and H atoms), for the disclenide 2 the crystal contains parallel chains built from either  $(R_{N1}, S_{N3})$  or  $(S_{N1}, R_{N3})$  isomers connected through weak contacts between the N(2) atom of a molecule and the aromatic H(3) atom of a neighbouring molecule [2.675(3) Å; *cf*.  $\sum r_{vdW}(N,H)$  2.74 Å<sup>9</sup>] which extend along the *b* axis.

Single-crystals suitable for X-ray diffraction studies were obtained from a CH<sub>2</sub>Cl<sub>2</sub>-n-hexane mixture for the halides **3**, **5** and **6**. Selected bond distances and angles are given in Table 2. The compound **3** crystallizes in the chiral space group  $P2_12_12_1$ (orthorhombic) and therefore the investigated crystal contains only the isomer *S*. The iodides **5** and **6** crystallize in monoclinic P2(1)/n and P2(1)/c space groups, respectively, and crystals contain 1 : 1 mixtures of *R* and *S* isomers. The ORTEP diagrams for the (*S*)-**3** and (*R*)-**6** isomers are shown in Fig. 3 and 4.



Fig. 3 ORTEP representation at 40% probability and atom numbering scheme for the (S)-3 isomer.

The solid-state molecular structures of **3**, **5** and **6** feature a similar amine arm strongly coordinated to the selenium centre *trans* to the selenium–halogen bond  $[N(1)–Se(1)–Cl(1) 175.92(6)^{\circ}$  in **3**; N(1)–Se(1)–I(1) **5**, 174.52(7)°; **6**, 176.76(12)°]. The decrease in the electronegativity of the halogen is reflected in the strength of the internal Se···N interactions [Se(1)–N(1) **3**, 2.204(2) Å; **5**, 2.291(3) Å; **6**, 2.282(4) Å], which are somewhat weaker than in the related  $[2-(Me_2NCH_2)C_6H_4]SeX$  derivatives  $[Se–N 2.135(4) Å,^5$  2.137(2) Å,<sup>6</sup> for X = Cl; 2.172(3) Å,<sup>5</sup> 2.167(3) Å,<sup>6</sup> for X = I]. As expected for a 3c–4e system, the linear arrangement of the N···Se–X unit results in the elongation of the Se–halogen bonds [Se(1)–Cl(1) 2.4270(8) Å in **3**; Se(1)–I(1) **5**, 2.7252(5) Å; **6**, 2.7148(8) Å] as observed in the related  $[2-(Me_2NCH_2)C_6H_4]SeX$ 

 Table 2
 Selected bond distances (Å) and angles (°) for compounds 3, 4 · HBr, 5 and 6

3		<b>4</b> ⋅HBr		5		6	
Se(1)–C(1)	1.929(2)	Se(1)–C(1)	1.934(8)	Se(1)–C(1)	1.930(3)	Se(1)–C(1)	1.928(6)
Se(1)-Cl(1)	2.4270(8)	Se(1)-Br(1) Se(1)-Br(2)	2.4389(18) 2.8043(15)	Se(1)–I(1)	2.7252(5)	Se(1)–I(1)	2.7148(8)
Se(1) - N(1)	2,204(2)	$\mathcal{D}(1)$ $\mathcal{D}(2)$	2.00 15(15)	Se(1) - N(1)	2 291(3)	Se(1) - N(1)	2,282(4)
56(1) 11(1)	2.204(2)	N(1) - H(2)	0.84(7)	56(1) 11(1)	2.291(3)	56(1) 11(1)	2.202(4)
		R(1) = H(2) Rr(2) = H(2)	2555(7)				
		Br(2) - H(2) - N(1)	163(6)				
N(1) - C(7)	1.478(3)	N(1) = C(7)	1501(11)	N(1) - C(7)	1.470(5)	N(1) - C(7)	1 471(8)
N(1) = C(8)	1.470(3) 1.480(3)	N(1) - C(8)	1.301(11) 1.481(11)	N(1) - C(8)	1.470(5) 1.481(5)	N(1) - C(8)	1.479(7)
N(1) = C(0) N(1) = C(11)	1.400(3)	N(1) - C(0) N(1) - C(11)	1.407(11)	N(1) - C(0) N(1) - C(11)	1.484(5)	N(1) - C(0) N(1) - C(11)	1.475(7) 1.465(7)
O(1) - C(9)	1.423(3)	O(1) - C(9)	1.492(12) 1.402(12)	O(1) - C(9)	1.404(5) 1.415(5)	N(2) - C(9)	1.409(7) 1.459(9)
O(1) - C(10)	1.428(3)	O(1) - C(10)	1.402(12) 1.308(11)	O(1) - C(10)	1.418(5)	N(2) - C(10)	1.455(9)
0(1)-0(10)	1.420(3)	O(1) - C(10)	1.570(11)	O(1) - C(10)	1.410(5)	N(2) - C(12)	1.453(9) 1.461(9)
C(1) Se(1) $C(1)$	95.07(8)	C(1) So(1) Br(1)	030(2)	C(1) S <sub>2</sub> (1) I(1)	97.24(11)	C(1) S <sub>2</sub> (1) I(1)	08 18(17)
C(1) = Sc(1) = Cl(1) C(1) = Sc(1) = N(1)	81 33(0)	C(1) = SC(1) = D1(1)	) 5.)(2)	C(1) = Sc(1) = I(1) C(1) = Sc(1) = N(1)	70.58(13)	C(1) = Sc(1) = I(1) C(1) = Sc(1) = N(1)	80.4(2)
N(1) = Sc(1) = N(1) N(1) = Sc(1) = C(1)	175 02(6)			N(1) = Sc(1) = In(1) N(1) $S_{0}(1) = I(1)$	174.52(7)	N(1) = Sc(1) - N(1) N(1) $S_{2}(1) = I(1)$	176.76(12)
I(1) = SC(1) = CI(1)	175.92(0)	C(1) So(1) Br(2)	85 4(2)	1(1) - 3c(1) - 1(1)	1/4.52(7)	1(1) - 3c(1) - 1(1)	170.70(12)
		C(1) - SC(1) - DI(2) Br(1) Se(1) Br(2)	177.34(6)				
$S_{e}(1) = N(1) = C(7)$	102 87(15)	DI(1) - SC(1) - DI(2)	177.54(0)	$S_{e}(1) = N(1) = C(7)$	99.8(2)	Se(1) = N(1) = C(7)	100.9(3)
Se(1) - N(1) - C(8)	102.07(15) 111.06(15)			Se(1) = N(1) = C(7) Se(1) = N(1) = C(8)	111.9(2)	Se(1) = N(1) = C(7) Se(1) = N(1) = C(8)	1122(4)
$S_{e}(1) = N(1) - C(0)$ $S_{e}(1) = N(1) - C(11)$	110.80(13)			$S_{e}(1) = N(1) - C(0)$ $S_{e}(1) = N(1) - C(11)$	111.9(2) 112.3(2)	$S_{e}(1) = N(1) = C(0)$ $S_{e}(1) = N(1) = C(11)$	112.2(4) 110 5(4)
C(7) = N(1) = C(11)	110.30(14) 110.7(2)	C(7) = N(1) = C(8)	112 0(8)	C(7) - N(1) - C(11)	112.3(2) 111 4(3)	C(7) = N(1) = C(11)	110.5(4) 111.5(5)
C(7) = N(1) - C(0) C(7) = N(1) - C(11)	110.7(2) 111.8(2)	C(7) = N(1) = C(0) C(7) = N(1) = C(11)	112.0(0) 112.8(7)	C(7) = N(1) = C(0) C(7) = N(1) = C(11)	1123(3)	C(7) = N(1) = C(0) C(7) = N(1) = C(11)	111.3(5) 110.7(5)
C(7) = N(1) = C(11) C(8) = N(1) = C(11)	111.0(2) 100 53(10)	C(7) = N(1) = C(11) C(8) = N(1) = C(11)	112.0(7) 100.7(7)	C(7) = N(1) = C(11) C(8) = N(1) = C(11)	112.3(3) 100 0(3)	C(7) = N(1) = C(11) C(8) = N(1) = C(11)	110.7(5) 110.6(5)
C(0) - N(1) - C(11) C(0) - O(1) - C(10)	109.33(19) 100.88(10)	C(0) - N(1) - C(11) C(0) - O(1) - C(10)	109.7(7) 111.8(8)	C(0) - N(1) - C(11) C(0) - O(1) - C(10)	109.0(3) 110.2(2)	C(0) = N(1) = C(11) C(0) = N(2) = C(10)	108.0(5)
C(9) = O(1) = C(10)	109.00(19)	C(9) = O(1) = C(10)	111.0(0)	C(9) = O(1) = C(10)	110.2(3)	C(9) = N(2) = C(10) C(0) = N(2) = C(12)	100.4(5) 111.2(6)
						C(3) = IN(2) = C(12) C(10) = N(2) = C(12)	110.8(7)
						C(10) = IN(2) = C(12)	110.0(7)



Fig. 4 ORTEP representation at 40% probability and atom numbering scheme for the (*R*)-6 isomer.

derivatives [Se–Cl 2.4757(7) Å,<sup>5</sup> 2.471(2) Å;<sup>6</sup> Se–I 2.8227(4) Å,<sup>5</sup> 2.8079(7) Å<sup>6</sup>]. They are considerably longer than those observed for [2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]SeX [Se–Cl 2.186(1) Å,<sup>19</sup> Se–I 2.529(1) Å<sup>20</sup>].

The strong intramolecular coordination of the nitrogen atom to the selenium centre results in a distorted T-shaped (*C*,*N*)SeX core (X = Cl, I; hypervalent 10-Se-3 species<sup>12</sup>) in compounds **3**, **5** and **6**, respectively. The deviation from the ideal N–Se–X angle of 180° is due to the constraints imposed by the coordinated amine arm.

Attempts to grow crystals of the bromide 4 resulted in isolation of the adduct RSeBr·HBr (4·HBr), probably obtained by partial hydrolysis of the compound. Selected bond distances and angles are given in Table 2. The molecular structure determination revealed that the nitrogen atom of the pendant arm is protonated [the H(2) atom was localised from the electron density map]. The Br(2) atom is bonded to the selenium center [Se(1)–Br(2) 2.8043(15) Å] in *trans* to the Br(1) atom [Br(1)–Se(1)–Br(2) 177.34(6)°] (Fig. 5), which results in a considerable shortening of the Se(1)–Br(1) bond [2.4389(18) Å] in comparison to the value found for the related [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]SeBr [2.634(1) Å<sup>8</sup>]. A hydrogen bond Br(2)…H(2) [2.555(7) Å] is established intramolecularly. The adduct can be described as a *zwitterionic* compound of the type [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N<sup>+</sup>(H)CH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]Se<sup>-</sup>Br<sub>2</sub>, with a distorted T-shaped CSeBr<sub>2</sub> core.

 $\begin{array}{c|cccc} C(1) & C(10) & O(1) \\ C(4) & C(3) & C(7) & & & \\ C(5) & C(2) & & & \\ C(5) & C(2) & & & \\ C(6) & & & & \\ C(6) & & & & \\ C(6) & & & & \\ C(1) & & & & \\ C(2) & & & & \\ C(3) & & & & \\ C(2) & & & & \\ C(3) & & & & \\ C(3) & & & & \\ C(4) & & & & \\ C(2) & & & & \\ C(3) & & & & \\ C(3) & & & & \\ C(2) & & & & \\ C(3) & & & \\ C(3$ 

**Fig. 5** ORTEP representation at 40% probability and atom numbering scheme for 4-HBr.

As for the diselenides 1 and 2, in the halides 3, 4-HBr, 5 and 6 the morpholinyl and piperazinyl rings exhibit a *chair* conformation which prevents further intramolecular coordination of the O(1) or the N(2) atom to the selenium center and thus a (C,N,Y)-monometallic triconnective pattern (Y = O, N) of the organic ligand.

Within the molecule of the chloride **3** and the iodides **5** and **6** there are interactions between the halogen atom and the proton *ortho* to selenium in the organic ligand [Cl(1) · · · H(6) 2.67 Å in **3**; I(1) · · · H(6) 2.96 Å and 2.87 Å in **5** and **6**, respectively; *cf*.  $\sum r_{vdW}(Cl,H)$  3.01 Å,  $\sum r_{vdW}(I,H)$  3.35 Å<sup>9</sup>].

In the crystals of **3**, **4**·HBr and **6** the discrete molecular units are separated by normal van der Waals distances between heavy atoms. A closer inspection of the crystal structures revealed different supramolecular architectures built through weak intermolecular interactions which involve hydrogen atoms. Thus, for the chloride **3** chains of *S* isomers are formed through  $Cl(1) \cdots H(7Bb)_{methylene}$  contacts [2.89 Å; cf.  $\sum r_{vdW}(Cl,H)$  3.01 Å<sup>9</sup>], which are further associated into layers through weak  $O(1) \cdots H(7Ab')_{methylene}$  (2.50 Å) and  $O(1) \cdots H(11Ab')_{N-methylene-ring}$  [2.56 Å; cf.  $\sum r_{vdW}(O,H)$  2.60 Å<sup>9</sup>] (Fig. 6).



Fig. 6 View of the layer network based on intermolecular hydrogen contacts (only hydrogens involved in intermolecular interactions are shown) in the crystal of 3 [symmetry equivalent atoms (-0.5 + x, 0.5 - y, -z), (0.5 + x, 0.5 - y, -z), (-0.5 + x, -0.5 - y, -z) and (0.5 + x, -0.5 - y, -z), -z) are given by "a", "b", "a prime" and "b prime"].

Significant differences are observed for the iodides **5** and **6**. In the crystal of **5** dimers of *R* and *S* isomers are formed through intermolecular Se(1) · · · I(1') [3.957(1) Å] and I(1) · · · H(9B') (3.28 Å) interactions [*cf*.  $\sum r_{vdW}(Se,I)$  4.15 Å,  $\sum r_{vdW}(I,H)$  3.35 Å<sup>9</sup>]. The dimers are associated through inter-dimer I(1) · · · H(5a') interactions (3.29 Å) into columnar chain polymers (Fig. 7a) which extend along the *c* axis. Further contacts between the morpholinyl oxygens and methylene protons [O(1) · · · H(7B) 2.51 Å]



Fig. 7 (a) View of the columnar chain polymer in the crystal of 5 based on hydrogen contacts between dimer units. (b) View along the c axis of the tridimensional network built from columnar chain polymers in the crystal of 5, through oxygen–hydrogen inter-chain contacts (only hydrogens involved in hydrogen contacts are shown).

(*cf*.  $\sum r_{vdW}(O,H)$  2.60 Å) of adjacent chain polymers result in a tridimensional network (Fig. 7b). By contrast, the crystal of **6** contains chain polymers in which alternating *S* and *R* isomers are connected through weak intermolecular I(1) ··· H(11Bb) (3.31 Å) interactions (Fig. 8) and no further inter-chain contacts are established.



Fig. 8 View along the a axis of the chain polymer of alternating S and R isomers in the crystal of 6 (only hydrogens involved in intermolecular contacts are shown).

The crystal of the adduct **4**·HBr also exhibits a tridimensional architecture based on weak hydrogen contacts. Contacts between bromine atoms and aryl and morpholinyl ring hydrogen atoms  $[Br(1)\cdots H(11B'') 3.02 \text{ Å}, Br(2)\cdots H(8Aa) 3.05 \text{ Å}, Br(2)\cdots H(4'') 3.06 \text{ Å}]$  result in a layer which extends along the *c* axis. Inter-layer contacts which involve the morpholinyl oxygen atoms and aryl protons  $[O(1)\cdots H(5') 2.37 \text{ Å}]$  led to the tridimensional network (see ESI†).

The NMR spectra for compounds **1–6** were recorded in CDCl<sub>3</sub>, at room and low temperature (-50 to +40 °C), or in C<sub>6</sub>D<sub>6</sub>, at room and high temperature (+26 to +79 °C). The assignment of the <sup>1</sup>H and <sup>13</sup>C chemical shifts was made according to the numbering schemes (**a**) and (**b**) (Scheme 2), respectively. These assignments are based on 2D experiments. For compounds **1** and **2**, the <sup>1</sup>H chemical shifts and the multiplicity of the signals belonging to the H-3, H-4, and H-5 atoms in the aromatic ring, could not be obtained from the <sup>1</sup>H-NMR spectra. Therefore, in these cases the relevant data have been obtained as 1D traces from the H,C-undecoupled-HSQC spectra.<sup>21</sup> Fig. 9 exemplifies such assignments in the spectrum of compund **1**.



**Fig.9** (a) The <sup>1</sup>H-NMR spectrum of compound **1**; HSQC traces extracted at the resonance frequencies for <sup>13</sup>C atoms in (b) C-4, (c) C-5, and (d) C-3 positions, respectively. The traces are displayed for the region around the low field <sup>13</sup>C satellite in the <sup>1</sup>H dimension.

The NMR data provide evidence for the presence of the intramolecular  $N \rightarrow Se$  interaction in solution. The strongest

evidence for such an interaction is provided by the H,Se-HMBC spectra. In these spectra there are strong cross peaks for the Se-H-8,11 and Se-H-9,10 resonances. It would be very difficult to admit such a through bond correlation between Se and H-9,10 (J coupling over seven bonds) in the absence of a Se-N bonding. The presence of the Se-N bonding reduces the Se-H-9,10 correlation to a J coupling over four bonds.

The alkyl region in the room-temperature <sup>1</sup>H NMR spectrum for the diselenide 1 exhibits two resonances for the H-8,11 and H-9,10 protons of the pendant arm ring. A similar pattern was observed for the free organic ligands [O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>5</sub> and [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}]C<sub>6</sub>H<sub>4</sub>Br.<sup>22</sup> This suggests a considerable weakness of the intramolecular  $N \rightarrow Se$  interaction which allows a fast conformational change of the six-membered morpholinyl ring in the molecule of **1**.

By contrast, at +26 °C, the <sup>1</sup>H spectra in CDCl<sub>3</sub> for the halides 3-5 exhibit a different pattern, *i.e.* three resonances—a multiplet (4H) for the H-9,10 protons ( $-CH_2-CH_2-O$ ), and a doublet (2H) and a doublet of doublets of doublets (2H) for the H-8,11 protons (N– $CH_2$ – $CH_2$ ). The non-equivalence of the protons in the N– $CH_2$ – $CH_2$  groups (H-8,11) is consistent with the presence of the intramolecular  $N \rightarrow Se$  interaction in solution, at room temperature, as found in the solid state. Such an interaction will prevent the fluxional behaviour  $A \rightarrow B$  described in Scheme 3, which would result in equivalent protons in the  $N-CH_2-CH_2$  and -CH<sub>2</sub>-CH<sub>2</sub>-O groups, respectively, following a process sequence which involves  $N \rightarrow Se$  dissocciation/Ar-CH<sub>2</sub>(N) bond rotation/N inversion/Ar-CH<sub>2</sub>(N) bond rotation/(Ar)CH<sub>2</sub>-N bond rotation/N  $\rightarrow$  Se association/morpholinyl ring conformation change [exchange of the (Ar)CH2-N bond from axial to equatorial position with respect to the six membered ring]. As result of the

> fluxional behavior

Scheme 3

Table 3 <sup>15</sup>N and <sup>77</sup>Se chemical shifts for compounds 1–6 and the corresponding Se–N distances (single-crystal X-ray data) ISNINIME & (mmm)

B

Compound	<sup>15</sup> N NMR $\delta_{ m N}$ (ppm)	<sup>77</sup> Se NMR $\delta_{\rm Se}$ (ppm)	Se–N distance/Å	
1	50.6ª	424.0ª	2.813(2)/2.825(3)	
2	$38.6 ({\rm NMe})^a$	425.4ª	3.135(3)/2.739(3)	
	37.3 (NMe), 50.9 (NCH <sub>2</sub> ) <sup>b</sup>	428.8 <sup>b</sup>		
3	66.9 <i>a</i>	945.0 <sup><i>a</i></sup>	2.204(2)	
4	68.6 <sup>a</sup>	892.1 <sup><i>a</i></sup>	~ /	
5	64.8 <sup><i>a</i></sup>	$702.0^{a}$	2.291(3)	
	63.1 <sup>b</sup>	687.7 <sup>b</sup>	~ /	
	63.1 <sup>c</sup>	$691.2^{\circ}$		
	$61.1^{d}$	677.3 <sup>d</sup>		
6	38.0 (NMe), 67.0 (NCH <sub>2</sub> ) <sup>a</sup>	e	2.282(4)	
	37.4 (NMe), 65.5 (NCH <sub>2</sub> ) <sup>b</sup>	e	~ /	
	35.3 (NMe), 63.4 (NCH <sub>2</sub> ) <sup><math>d</math></sup>	$700.0^{b}$		

<sup>a</sup> At +26 °C, in CDCl<sub>3</sub>. <sup>b</sup> At +60 °C, in CDCl<sub>3</sub>. <sup>c</sup> At +26 °C, in C<sub>6</sub>D<sub>6</sub>. <sup>d</sup> At +65 °C, in C<sub>6</sub>D<sub>6</sub>. <sup>e</sup> Not observed.

New RSe-SeR (R = 2-[O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>, 2-[MeN- $(CH_2CH_2)_2NCH_2]C_6H_4$ ) and RSeX (X = Cl, Br, I) were investigated in solution and the solid state. Evidence for the N  $\rightarrow$ Se interactions in solution were obtained from NMR studies. In all cases T-shaped coordination geometries, i.e. (C,N)SeSe, (C,N)SeX (X = halogen) or CSeBr<sub>2</sub>, were found in the solid state. Supramolecular associations in crystals based on hydrogen contacts are discussed.

The most upfield shifted <sup>1</sup>H signal ( $\delta$  2.68 ppm for 3 and 2.64 ppm for 4) was assigned to pro-trans-H-8,11 (H<sub>b</sub>) protons. It is split due to the proton-proton coupling with the geminal procis-H-8,11 (H<sub>a</sub>) protons, as well as the pro-cis-H-9,10 (H<sub>d</sub>) and pro-*trans*-H-9,10 ( $H_c$ ) protons of the neighbouring CH<sub>2</sub> group. The resonance due to the pro-cis-H-8,11 (H<sub>a</sub>) protons is more deshielded ( $\delta$  3.12 ppm for **3** and 3.10 ppm for **4**) due to the proximity of the electronegative SeCl moiety. Only the coupling with the geminal proton is observed in this case. It is worthwhile to note here that the <sup>1</sup>H NMR spectra of  $[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]Li$ and [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]Ti(Cp)Cl<sub>2</sub> (-50 °C, in toluened<sub>6</sub>) were reported to exhibit a similar pattern.<sup>22</sup>

For the iodide 5 the room temperature <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> exhibits two broad singlets for H-8,11 protons (coalescence), but at -30 °C the pattern of the alkyl region becomes similar to that observed for the chloride 3 and the bromide 4, at room temperature.

The solution behavior of the iodide 6 at room temperature is similar to that of the iodide 5 (three unresolved broad signals for H-9,10 and H-8,11 protons in the <sup>1</sup>H NMR spectrum), while at -40 °C the resonances are resolved, *i.e.* a triplet for all four H-9,10 protons, and an AB system for the pro-trans-H-8,11 and pro-cis-H-8,11 protons. This behavior is consistent with a similar fluxional process as described above for the morpholinyl analogs.

The <sup>15</sup>N chemical shifts are considerably dependent on the electron delocalization of the nitrogen lone pair<sup>23</sup> and are thus useful for estimation of the intramolecular  $N \rightarrow Se$  interactions. For compounds 1-6 the <sup>15</sup>N chemical shifts (Table 3) follow the trend observed for the related compounds containing the  $[2-(CyMeNCH_2)C_6H_4]$ Se fragment,<sup>24</sup> *i.e.* the  $\delta_N$  for the NCH<sub>2</sub> nitrogen in the halides **3–6** is shifted downfield with respect to the corresponding diselenides **1** and **2**, consistent with the increase in the strength of the N  $\rightarrow$  Se interaction. It should be mentioned here that for compound **2** the two expected <sup>15</sup>N resonances could be observed only at +60 °C, in CDCl<sub>3</sub>, while at room temperature the H,N-HMBC spectrum exhibited only the resonance ( $\delta$  38.6 ppm) for the NMe nitrogen. This is due to the continuous variation of the H–N coupling constants on the time scale of the NMR experiment. Thus, the only visible cross peak at room temperature is for N–H-12 (in the NMe group) for which the coupling constant remains unchanged during the ring inversion.

The <sup>77</sup>Se chemical shifts for compounds 1-6 (Table 3) are also consistent with the presence of the intramolecular  $N \rightarrow Se$ interaction in solution. The <sup>77</sup>Se chemical shifts for the diselenides 1 (424.0 ppm) and 2 (425.4 ppm) are of the same magnitude as reported for the related [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se<sub>2</sub> (430 ppm),<sup>8</sup> [2-(CyMeNCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Se<sub>2</sub> (431.9 ppm),<sup>24</sup> and R<sub>2</sub>Se<sub>2</sub> (454.8 ppm; R = 2-(4,4-dimethyl-2-oxazolinyl)phenyl).<sup>11</sup> A large deshielding is observed for the halides 3-6 with respect to the diselenides 1 and **2**. The trend followed by the  $\delta_{se}$ , in CDCl<sub>3</sub> at room temperature, is RSeCl (3) (944.7 ppm) > RSeBr (4) (893.4 ppm) > RSeI (5) (702.0 ppm), consistent with the increased deshielding of the selenium resonances as the electronegativity of the attached substituent increases.25 A similar trend for the 77 Se resonances was reported for  $[2-(Me_2NCH_2)C_6H_4]$ SeX ( $\delta_{se}$  1030 ppm, X = Cl;<sup>5</sup> 987 ppm,  $X = Br;^{8} 818$  ppm,  $X = I^{8}$ ), [2-(CyMeNCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]SeX  $(\delta_{se} \ 1051.3 \text{ ppm}, \ X = Cl; \ 1011.2 \text{ ppm}, \ X = Br)^{24} \text{ or } RSeX$ [R = 2-(4,4-dimethyl-2-oxazolinyl)phenyl] ( $\delta_{se}$  855.9 ppm, X = Cl; 849.5 ppm, X = Br; 762.2 ppm, X = I),<sup>11</sup> for which the presence of the internal  $N \rightarrow Se$  interaction in solution was well documented by multinuclear NMR studies. For compound 6 the <sup>77</sup>Se resonance in the H,Se-HMBC spectrum could be observed only at +65 °C, in  $C_6D_6$ . The same explanation as in the case of the N,H-HMBC spectrum discussed above, holds true. The differences in the values reported for the <sup>77</sup>Se chemical shifts indicates that, in addition to the effect of the halogen atom, the nature of the organic group attached to selenium can exhibit a considerable contribution and this effect should be considered when comparisons are made between NMR parameters observed for different series of compounds.

# Conclusions

New diselenides, R<sub>2</sub>Se<sub>2</sub>, and halides, RSeX, containing the [2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}(E=O, NMe)$  moieties were prepared and their hypervalent nature was investigated both in solution and in the solid state. The H,Se-heteronuclear NMR correlations provided evidence for the presence of the intramolecular N  $\rightarrow$ Se interaction in solution for the organoselenium compounds investigated in this work. The variable temperature NMR data suggest that these interactions in solution are stronger for the organoselenium(II) chloride and bromide, and weaker in the cases of the iodides and diselenide derivatives. In the solid state all investigated compounds exhibit a T-shaped coordination geometry, *i.e.* (C,N)SeSe for  $[2-{E(CH_2CH_2)_2NCH_2}C_6H_4]_2Se_2[E=O(1), NMe$ (2)], (C,N)SeX for the halides  $[2-\{E(CH_2CH_2)_2NCH_2\}C_6H_4]$ SeX [E = O, X = Cl (3), I (5); E = NMe, X = I (6)], or CSeBr<sub>2</sub> for [2- $\{O(CH_2CH_2)_2NCH_2\}C_6H_4]$ SeB·HBr (4·HBr). Discrete molecules are present in the crystal of the diselenide 1. Dimer associations

between R- and S-5 isomers are formed through intermolecular Se  $\cdots$  I interactions. For all compounds, except 1, supramolecular architectures are built through intermolecular contacts between hydrogen atoms and heavier electronegative (halogen, oxygen) atoms.

## Experimental

#### General procedures

Most of the 1D and all of the 2D NMR spectra have been recorded in dried solvents on a Bruker Avance DRX 400 instrument, equipped with a 5 mm multinuclear inverse detection z-gradient probehead, operating at 400.1, 100.6, 46.5, and 76.3 MHz for <sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N, and <sup>77</sup>Se nuclei, respectively. Low temperature <sup>1</sup>H NMR spectra for 5 and 6 were recorded on a Bruker Avance 300 spectrometer operating at 300.1 MHz. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of solvent (ref.: CHCl<sub>3</sub>, <sup>1</sup>H, 7.26 ppm; CDCl<sub>3</sub>, <sup>13</sup>C, 77.0 ppm; C<sub>6</sub>H<sub>6</sub>, <sup>1</sup>H, 7.16 ppm; C<sub>6</sub>D<sub>6</sub>, <sup>13</sup>C, 128.06 ppm). H,H-COSY, H,C-HSQC and H,C-HMBC experiments, were recorded using standard pulse sequences in the version with z-gradients, as delivered by Bruker with TopSpin 1.3 PL6 spectrometer control and processing software. H,C-undecoupled-HSQC experiments have been recorded using the pulse sequence described by Simova.<sup>21</sup> The <sup>15</sup>N chemical shifts were obtained as projections from the 2D indirectly detected H,N-HMBC spectra, using a standard pulse sequence in the version with z-gradients as delivered by Bruker (TopSpin 1.3 PL6) and are referred to external liquid ammonia (0.0 ppm) using as external standard nitromethane (380.2 ppm). The <sup>77</sup>Se chemical shifts were obtained as projections from the 2D indirectly detected H,Se-HMBC spectra, using a standard pulse sequence in the version with z-gradients (60 : 20 : 55.3% gradient ratios) and are referred to external dimethylselenide (0.0 ppm) using as external standard dimethyldiselenide (275.0 ppm).<sup>26</sup> Elemental analyses were performed by Facultatea de Farmacie, Universitatea de Medicina si Farmacie "Iuliu Hatieganu", Cluj-Napoca (Romania). All manipulations were carried out under an inert atmosphere of argon (Linde, 99.999%) using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. Selenium and butyllithium (1.6 M in hexane) were commercially available. The organic bromides used as starting materials were prepared according to the published methods: 2-[O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br,<sup>22</sup> 2- $[MeN(CH_2CH_2)_2NCH_2]C_6H_4Br.^{27}$ 

#### Syntheses

Synthesis of  $[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]_2Se_2$  (1). A solution of BuLi in hexane (6.4 mL, 1.6 M, 10.0 mmol) was added dropwise, at room temperature, under argon to a stirred solution of 2- $[O(CH_2CH_2)_2NCH_2]C_6H_4Br$  (2.561 g, 10.0 mmol) in 100 mL anhydrous diethyl ether. The reaction mixture was stirred at room temperature for 24 h, when a white slurry of the lithiated product was obtained. Elemental selenium powder (0.79 g, 10.0 mmol) was added under argon and the stirring was continued for 0.5 h. The resulting yellowish solution was poured into a beaker containing saturated aqueous NaHCO<sub>3</sub> (100 mL) and left overnight in an efficient fume hood to effect complete oxidation. The compound was extracted with methylene dichloride (3 × 50 mL) and the

combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum to give a yellow oil. The oily product was dissolved in the minimum amount of anhydrous diethyl ether (5 mL), layered with hexane and kept at -28 °C. After a few weeks the title compound 1 separated as a yellow, crystalline solid which was filtered off and dried under vacuum (1.6 g, 63%), mp 96-98 °C. Anal. Calcd for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>Se<sub>2</sub> (510.40): C, 51.77; H, 5.53; N, 5.49; Found: C 51.55; H, 5.43; N, 5.27%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, +26 °C): δ 2.50 (8 H, s,br, H-8,11, N–CH<sub>2</sub>–CH<sub>2</sub>–O), 3.61 (4 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 3.72 (8 H, t, H-9,10, N-CH<sub>2</sub>-CH<sub>2</sub>-O,  ${}^{3}J_{\rm HH}$  4.6 Hz), 7.07–7.20 (6 H, m, C<sub>6</sub>H<sub>4</sub>) [resolved in HSQC as: 7.16 (2 H, t, H-4,  ${}^{3}J_{HH}$  7.1 Hz), 7.19 (2 H, d, H-3,  ${}^{3}J_{HH}$  7.1 Hz), 7.19  $(2 \text{ H}, \text{t}, \text{H-5}, {}^{3}J_{\text{HH}} 7.1 \text{ Hz})], 7.80 (2 \text{ H}, \text{dt}, \text{H-6}, \text{C}_{6}\text{H}_{4}, {}^{3}J_{\text{HH}} 6.4, {}^{4}J_{\text{HH}})$ 1.6 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, +26 °C): δ 52.50 (s, C-8,11), 63.65 (s, C-7), 67.00 (s, C-9,10), 125.86 (s, C-4), 128.34 (s, C-5), 128.79 (s, C-3), 131.50 (s, C-6), 134.07 (s, C-1), 138.10 (s, C-2).

Synthesis of  $[2-\{MeN(CH_2CH_2)_2NCH_2\}C_6H_4]_2Se_2$  (2). A solution of BuLi in hexane (3.50 mL, 1.6 M, 5.6 mmol) was added dropwise, at room temperature, under argon to a stirred solution of 2-[MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (1.51 g, 5.6 mmol) in 100 mL anhydrous hexane. The reaction mixture was stirred, under reflux, for 4 h and then allowed to reach room temperature. Evaporation of the solvent gave  $[2-\{MeN(CH_2CH_2)_2NCH_2\}C_6H_4]Li$  as a white compound. The solid was dissolved in 100 mL anhydrous THF, elemental selenium powder (0.44 g, 5.6 mmol) was added and the reaction mixture was stirred for 1 h at room temperature, under argon. The resulting yellowish solution was poured into a beaker containing saturated aqueous NaHCO<sub>3</sub> (100 mL) The compound was extracted with methylene dichloride (3  $\times$  50 mL) and the combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent under vacuum gives 2 (0.6 g, 40%) as a yellow solid, mp 111-113 °C. Anal. Calcd for C<sub>24</sub>H<sub>34</sub>N<sub>4</sub>Se<sub>2</sub> (536.48): C, 53.73; H, 6.39; N, 10.44; Found: C, 53.51; H, 6.12; N, 10.24%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, +26 °C): δ 2.30 (6 H, s, NCH<sub>3</sub>), 2.49, 2.54 (16 H, br, H-8,9,10,11, N-CH2-CH2-N) (at +60 °C, this resonance is resolved into 2 broad doublets at 2.48 and 2.54 ppm for H-9,10 and H-8,11, respectively), 3.62 (4 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 7.07-7.18 (6 H, m, C<sub>6</sub>H<sub>4</sub>) [resolved in HSQC as: 7.11 (2 H, t, H-4,  ${}^{3}J_{HH}$  7.4 Hz), 7.14 (2 H, d, H-3,  ${}^{3}J_{HH}$  7.4 Hz), 7.14 (2 H, t, H-5, <sup>3</sup>*J*<sub>HH</sub> 7.4 Hz)], 7.80 (2 H, dd, H-6, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>HH</sub> 7.8, <sup>4</sup>J<sub>HH</sub> 1.4 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, +26 °C): δ 45.89 (s, NCH<sub>3</sub>), 51.91 (s, C-8,11), 55.01 (s, C-9,10), 63.19 (s, C-7), 125.74 (s, C-4), 128.21 (s, C-5), 128.64 (s, C-3), 131.41 (s, C-6), 134.12 (s, C-1), 138.55 (s, C-2).

**Synthesis of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]SeCl (3).** A solution of compound 1 (1.108 g, 2.17 mmol) in 100 mL CCl<sub>4</sub> was treated dropwise with a solution of SO<sub>2</sub>Cl<sub>2</sub> (0.293 g, 2.17 mmol) in 100 mL CCl<sub>4</sub>, at room temperature. The reaction mixture was stirred for 4 h, then the resulting solid was filtered off and washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–n-hexane (1 : 5, v/v) gives the title compound as pale yellow crystals (0.88 g, 70%), mp 152–154 °C. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>ClNOSe (290.65): C, 45.46; H, 4.86; N, 4.82; Found: C 45.26; H, 4.75; N, 4.91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, +26 °C): δ 2.69 (2 H, ddd, pro-*trans*-H-8,11, N–CH<sub>2</sub>–CH<sub>2</sub>–O, <sup>2</sup>J<sub>HH</sub> 12.5, <sup>3</sup>J<sub>HH</sub> 10.7, <sup>3</sup>J<sub>HH</sub> 4.3 Hz), 3.12 (2 H, d, pro-*cis*-H-8,11, N–CH<sub>2</sub>–CH<sub>2</sub>–O, <sup>2</sup>J<sub>HH</sub> 11.6 Hz), 3.90 (4 H, m, H-9,10, N–CH<sub>2</sub>–CH<sub>2</sub>–O), 3.94 (2 H, s, H-7, C<sub>6</sub>H<sub>4</sub>–CH<sub>2</sub>–N), 7.17 (1 H, dd, H-3, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.2, <sup>4</sup>J<sub>HH</sub> 1.2 Hz), 7.20 (1 H, td, H-4, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.3, <sup>4</sup>J<sub>HH</sub> 0.9 Hz), 7.35 (1 H, td, H-5, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.6, <sup>4</sup>J<sub>HH</sub> 1.6 Hz),

8.09 (1 H, d, H-6, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{\rm HH}$  8.0 Hz).  ${}^{13}$ C NMR (CDCl<sub>3</sub>, +26 °C):  $\delta$  54.41 (s, C-8,11), 65.12 (s, C-7), 65.26 (s, C-9,10), 125.63 (s, C-3), 126.34 (s, C-4), 129.12 (s, C-5), 129.17 (s, C-6), 133.87 (s, C-2), 136.23 (s, C-1).

Synthesis of  $[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]SeBr$  (4). A solution of compound 1 (0.41 g, 0.8 mmol) in 50 mL CHCl<sub>3</sub> was treated dropwise with a solution of bromine (0.128 g, 0.8 mmol) in 10 mL CHCl<sub>3</sub>, at 0 °C. The reaction mixture was stirred at 0 °C for additional 2 h, then it was allowed to reach room temperature and the solvent was removed under vacuum. The resulting solid was washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-n-hexane (1:5, v/v) gives the title compound as yellow crystals (0.37 g, 69%), mp 167–169 °C. Anal. Calcd for  $C_{11}H_{14}BrNOSe$  (335.10): C, 39.43; H, 4.21; N, 4.18; Found: C, 39.45; H, 4.11; N, 3.97%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, +26 °C): δ 2.65 (2 H, ddd, pro-*trans*-H-8,11, N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>HH</sub> 12.6, <sup>3</sup>J<sub>HH</sub> 9.7, <sup>3</sup>J<sub>HH</sub> 5.2 Hz), 3.10 (2 H, d, pro-cis-H-8,11, N-CH2-CH2-O, <sup>2</sup>J<sub>HH</sub> 12.7 Hz), 3.89 (2 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 3.91 (4 H, m, H-9,10, N-CH<sub>2</sub>-CH<sub>2</sub>-O), 7.13 (1 H, d, br, H-3, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 8.0 Hz), 7.21 (1 H, td, H-4, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.4, <sup>4</sup>*J*<sub>HH</sub> 1.0 Hz), 7.32 (1 H, td, H-5, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>HH</sub> 8.4, <sup>4</sup>*J*<sub>HH</sub> 1.4 Hz), 8.12 (1 H, dd, H-6,  $C_6H_4$ ,  ${}^3J_{HH}$  8.0,  ${}^4J_{HH}$  0.4 Hz).  ${}^{13}C$  NMR (CDCl<sub>3</sub>, +26 °C): δ 54.18 (s, C-8,11), 65.02 (s, C-7), 65.60 (s, C-9,10), 125.83 (s, C-3), 126.50 (s, C-4), 129.33 (s, C-5), 131.54 (s, C-6), 134.21 (s, C-1), 134.45 (s, C-2).

Synthesis of  $[2-{O(CH_2CH_2)_2NCH_2}C_6H_4]$ SeI (5). A solution of compound 1 (0.51 g, 1.0 mmol) in 20 mL CHCl<sub>3</sub> was treated dropwise with a solution of iodine (0.254 g, 1.0 mmol) in 40 mL CCl<sub>4</sub>, at 0 °C. The reaction mixture was stirred at 0 °C for an additional 2 h, then it was allowed to reach room temperature and the solvent was removed under vacuum. The resulting solid was washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-n-hexane (1: 5, v/v) gives the title compound as red crystals (0.53 g, 69%), mp 136–137 °C. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>INOSe (382.10): C, 34.58; H, 3.69; N, 3.67; Found: C, 34.37; H, 3.49; N, 3.53%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, +26 °C):  $\delta$  2.49–2.91 (4 H, br, H-8,11) (at +60 °C, this resonance appears as a singlet at 2.69 ppm), 3.72 (2 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 3.86 (4 H, t, H-9,10, N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>3</sup>J<sub>HH</sub> 4.8 Hz), 7.06 (1 H, d, br, H-3, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 6.8 Hz), 7.20 (1 H, td, H-4, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.3, <sup>4</sup>J<sub>HH</sub> 1.3 Hz), 7.25 (1 H, td, H-5, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.6,  ${}^{4}J_{\rm HH}$  1.6 Hz), 8.05 (1 H, dd, H-6, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{\rm HH}$  7.8,  ${}^{4}J_{\rm HH}$  1.4 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, -30 °C): δ 2.47 (2 H, ddd, pro-*trans*-H-8,11, N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>HH</sub> 12.1, <sup>3</sup>J<sub>HH</sub> 10.4, <sup>3</sup>J<sub>HH</sub> 4.2 Hz), 2.95 (2 H, d, pro-cis-H-8,11, N-CH<sub>2</sub>-CH<sub>2</sub>-O, <sup>2</sup>J<sub>HH</sub> 12.4 Hz), 3.72 (2 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 3.82 (4 H, m, H-9,10, N-CH<sub>2</sub>-CH<sub>2</sub>-O), 7.04 (1 H, dd, H-3,  $C_6H_4$ ,  ${}^{3}J_{HH}$  6.5,  ${}^{4}J_{HH}$  1.8 Hz), 7.18 (2 H, m, H-4,5,  $C_6H_4$ ), 7.98 (1 H, dd, H-6, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.1, <sup>4</sup>J<sub>HH</sub> 1.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, +26 °C): δ 53.42 (s, C-8,11), 64.34 (s, C-7), 66.05 (s, C-9,10), 126.42 (s, C-3), 126.52 (s, C-4), 129.27 (s, C-5), 130.41 (s, C-1), 135.90 (s, C-6), 136.11 (s, C-2).

Synthesis of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]SeI (6). A solution of compound 2 (0.5 g, 0.93 mmol) in 100 mL CCl<sub>4</sub> was treated dropwise with a solution of iodine (0.23 g, 0.93 mmol) in 100 mL CCl<sub>4</sub>, at room temperature. The reaction mixture was stirred for 4 h, then the red solution was concentrated under vacuum until a red solid deposited. The solid was filtered off and was washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–n-hexane (1 : 5, v/v) gives the title compound as red crystals (0.50 g, 68%), mp 160 °C

	1	2	3	4·HBr	5	6
Empirical formula	$C_{22}H_{28}N_2O_2Se_2$	$C_{24}H_{34}N_4Se_2$	C <sub>11</sub> H <sub>14</sub> ClNOSe	C <sub>11</sub> H <sub>15</sub> Br <sub>2</sub> NOSe	C <sub>11</sub> H <sub>14</sub> INOSe	$C_{12}H_{17}IN_2Se$
M	510.38	536.47	290.64	416.02	382.09	395.14
T/K	297(2)	297(2)	297(2)	293(2)	297(2)	297(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P2(1)/n	$P2_{1}2_{1}2_{1}$	$Pna2_1$	$P2_1/n$	$P2_{1}/c$
a/Å	12.0689(14)	15.7733(13)	8.476(2)	16.141(2)	8.2818(7)	7.8591(13)
b/Å	18.435(2)	9.5329(8)	8.939(2)	12.6448(16)	14.3309(12)	15.772(3)
c/Å	10.1788(12)	17.4030(14)	15.576(4)	6.9126(9)	10.7167(9)	11.3391(19)
a/°	90	90	90	90	90	90
β/°	93.069(2)	110.053(2)	90	90	97.3370(10)	96.523(3)
y/°	90	90	90	90	90	90
$V/Å^3$	2261.5(5)	2458.2(4)	1180.1(6)	1410.9(3)	1261.50(18)	1396.4(4)
Absorption correction	Multi-scan <sup>30</sup>	Multi-scan <sup>30</sup>	Multi-scan <sup>30</sup>	Multi-scan <sup>30</sup>	Multi-scan <sup>30</sup>	Multi-scan <sup>30</sup>
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	3.289	3.026	3.381	8.306	5.399	4.878
$R1 \left[ I > 2\sigma(I) \right]$	0.0497	0.0470	0.0227	0.0685	0.0318	0.0566
wR2	0.1024	0.1001	0.0519	0.1244	0.0652	0.1133
GOF on $F^2$	1.126	1.093	1.110	1.173	1.174	1.264

Table 4Crystallographic data for compounds 1–3, 4·HBr, 5 and 6

(decomp.). Anal. Calcd for C<sub>12</sub>H<sub>17</sub>IN<sub>2</sub>Se (395.14): C, 36.48; H, 4.34; N, 7.09; Found: C, 36.23; H, 4.11; N, 6.83%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, +26 °C):  $\delta$  2.37 (3 H, s, NCH<sub>3</sub>), 2.50–3.00 (8 H, br, H-8,9,10,11, N-CH2-CH2-NMe) (at +60 °C, this resonance is resolved into 2 singlets at 2.66 and 2.81 ppm for H-9,10 and H-8,11, respectively), 3.74 (2 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 7.05 (1 H, dd, H-3, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.2, <sup>4</sup>J<sub>HH</sub> 0.9 Hz), 7.19 (1 H, td, H-4, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>HH</sub> 7.3, <sup>4</sup>*J*<sub>HH</sub> 1.3 Hz), 7.23 (1 H, td, H-5, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>*J*<sub>HH</sub> 7.8, <sup>4</sup>*J*<sub>HH</sub> 1.8 Hz), 8.07 (1 H, dd, H-6, C\_6H<sub>4</sub>,  $^3J_{\rm HH}$  8.0,  $^4J_{\rm HH}$  1.2 Hz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, -40 °C):  $\delta$  2.32 (3 H, s, NCH<sub>3</sub>), 2.46 (4H, t, H-9,10, N-CH<sub>2</sub>-CH<sub>2</sub>-NMe, <sup>3</sup>J<sub>HH</sub> 7.5 Hz), 2.78 (2 H, d, pro-trans-H-8,11, N-CH2-CH2-NMe, <sup>2</sup>J<sub>HH</sub> 9.3 Hz), 3.07 (2 H, d, pro-cis-H-8,11, N-CH<sub>2</sub>-CH<sub>2</sub>-NMe, <sup>2</sup>J<sub>HH</sub> 9.1 Hz), 3.74 (2 H, s, H-7, C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>-N), 7.04 (1 H, dd, H-3, C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 6.4, <sup>4</sup>J<sub>HH</sub> 1.3 Hz), 7.18 (2 H, m, H-4,5 C<sub>6</sub>H<sub>4</sub>), 8.01 (1 H, dd, H-6, C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{HH}$  7.0,  ${}^{4}J_{HH}$  1.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, +26 °C):  $\delta$  45.55 (s, NCH<sub>3</sub>), 53.28 (s, C-8,11), 53.83 (s, C-9,10), 63.91 (s, C-7), 126.19 (s, C-3), 126,46 (s, C-4), 129.19 (s, C-5), 130.70 (s, C-1), 135.84 (s, C-6), 136.34 (s, C-2).

## Crystal structures

The details of the crystal structure determination and refinement for compounds 1–3, 4·HBr, 5 and 6 are given in Table 4. Data were collected on Bruker SMART APEX diffractometer, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). For this purpose the crystals were attached with epoxy glue on cryoloops and the data were collected at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atom attached to nitrogen in 4·HBr was located from the difference map. The other hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.<sup>28</sup> The drawings were created with the Diamond program.<sup>29</sup>

CCDC reference numbers 619306 (1), 608161 (2), 608159 (3), 619305 (4·HBr), 608162 (5) and 608160 (6).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702629c

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