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Organoselenium(II) and selenium(IV) compounds containing 2-$(Me_2NCH_2)C_6H_4$ moieties: solution behavior and solid state structure

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Dedicated to Professor Hans Joachim Breunig on the occasion of his 60th birthday

Abstract

The cleavage of the Se–Se bond in $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ (**1**) was achieved by treatment with SO_2Cl_2 (1:1 molar ratio) or elemental halogens to yield $[2\text{-}(Me_2NCH_2)C_6H_4]SeX$ [X = Cl (**2**), Br (**3**), I (**4**)]. Oxidation of **1** with SO_2Cl_2 (1:3 molar ratio) gave $[2\text{-}(Me_2NCH_2)C_6H_4]SeCl_3$ (**5**). $[2\text{-}(Me_2NCH_2)C_6H_4]SeS(S)CNR_2$ [R = Me (**6**), Et (**7**)] were prepared by reacting $[2\text{-}(Me_2NCH_2)C_6H_4]SeBr$ with $Na[S_2CNR_2]\cdot nH_2O$ (R = Me, $n = 2$; R = Et, $n = 3$). The reaction of **3** with $K[(SPMe_2)(SPPh_2)N]$ resulted in isolation of $[2\text{-}(Me_2NCH_2)C_6H_4]Se\text{–}S\text{–}PMe_2{=}N\text{–}PPh_2{=}S$ (**8**). The compounds were characterized by solution NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{77}Se, 2D experiments). The solid-state molecular structures of **2**, **4**–**8** were established by single crystal X-ray diffraction. All compounds are monomeric, with the N atom of the pendant CH_2NMe_2 arm involved in a three-center-four-electron N···Se–X (X = halogen, S) bond. This results in a T-shaped coordination geometry for the Se(II) atom in **2**, **4**, **6**–**8**. In **5**, the Se(IV) atom achieves a square pyramidal coordination in the mononuclear unit. Loosely connected dimers are formed through intermolecular Se···Cl interactions (3.40 Å); the overall coordination geometry being distorted octahedral. In all compounds hydrogen bonds involving halide or sulfur atoms generate supramolecular associations in crystals.
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1. Introduction

The chemistry of organoselenium compounds stabilized by the stereoelectronic effect of an intramolecular Se···X (X = N, O, S) nonbonded interaction has been the subject of increasing interest in recent years [1,2]. In particular, for Se compounds derived from *N*,*N*-diorganobenzylamine and related ligands in which the nitrogen atom of the pendant arm is able to establish internal Se···N interactions, the recent advances are due to their potential applications, e.g. for asymmetric synthesis in organic and organometallic chemistry [2–11], catalytic antioxidant activity, enzyme mimics and chemotherapeutic agents [12–16]. It was shown that such internal interactions play an important role in chirality transfer in asymmetric reactions. The stabilizing effect of internal chelating groups in close proximity to selenium was also

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used for the isolation of exotic species such as the covalent azide [2-(Me_2NCH_2)C_6H_4]SeN_3 [17] or the preparation of monomeric metal chalcogenolates [18,19]. In spite of this obvious interest only a few RSeX (X = halogen) derivatives containing *ortho*-selenurated benzylamino and related moieties have been investigated so far by single crystal X-ray diffraction, i.e. [2-(Me_2NCH_2)C_6H_4]SeBr [20], the adducts [2-(CyMeNCH$_2$)C_6H_4]SeX · HX (Cy = cyclohexyl, X = Cl, Br) (better described as ammonium salts of the type [{2-(CyMeHNCH$_2$)C_6H_4}SeX]$^+$[X]$^-$, which do not contain an intramolecular Se···N interaction) [21] and the copper complex [[2-{2-($NC_5H_4CH_2CH_2)_2NCH_2$}C_6H_4]-SeCl]$_2$($CuCl_2$)$_2$ [22]. The electronic structure around the selenium atom and the strength of the Se···N interaction in [2-(Me_2NCH_2)C_6H_4]SeCl were also investigated by computational methods at various basis set levels [17,22,23]. On the other hand a check of the Cambridge Structural Database (CSD) [24] for a $CSeX_3$ (X = halogen) fragment revealed that the molecular structure of only three organoselenium(IV) trichlorides were so far reported, i.e. CF_3SeCl_3 [25], 1,2-$C_6H_4(SeCl_3)_2$ [26] and 3, 5-Pr^i_2-4-$(Me_3Si)_2N$–$C_6H_2SeCl_3$ [27].

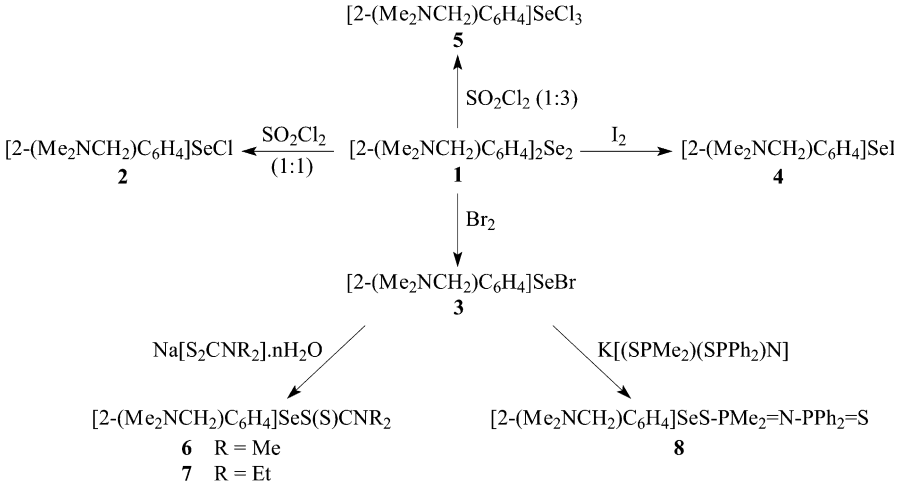
Our interest in the investigation of hypervalent compounds of main group elements led us to the synthesis of [2-(Me_2NCH_2)C_6H_4]SeX [X = Cl (**2**), I (**4**)], for which the molecular structures are discussed herein, together with that of the new organoselenium(IV) trichloride, [2-(Me_2NCH_2)C_6H_4]$SeCl_3$ (**5**). It should be mentioned that while this work was in progress the CIF files for molecular structures of [2-(Me_2NCH_2)C_6H_4]SeX (X = Cl, I) became available as supplementary material for the work reported by Klapötke and Co., and the structures were briefly discussed [17]. In order to investigate the competition for internal coordination to the selenium centre when different donor atoms are available and the structural changes when the "bite" size of a potential chelating dithioligand is varied, [2-(Me_2NCH_2)C_6H_4]SeS(S)CNR_2 [R = Me (**6**), Et (**7**)] and [2-(Me_2NCH_2)C_6H_4]Se–S–PMe_2=N–PPh_2=S (**8**) were prepared. Their molecular structures were also established by single-crystal X-ray diffraction and are compared with those recently reported for [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 (R = Ph, OPr^i) [28].

2. Results and discussion

2.1. Preparation

The organoselenium(II) halides, [2-(Me_2NCH_2)-C_6H_4]SeX [X = Cl (**2**), Br (**3**), I (**4**)] and organoselenium(IV) trichloride, [2-(Me_2NCH_2)C_6H_4]$SeCl_3$ (**5**), were prepared in good yields by the cleavage of the Se–Se bond in [2-(Me_2NCH_2)C_6H_4]$_2Se_2$ (**1**) with elemental halogens or SO_2Cl_2 (1:1 and 1:3 molar ratio), at room temperature, in carbon tetrachloride (Scheme 1). Reactions of **3** with stoichiometric amounts of alkali metal salts of the dithioligands afford the isolation of [2-(Me_2NCH_2)C_6H_4]SeS(S)CNR_2 [R = Me (**6**), Et (**7**)] and [2-(Me_2NCH_2)C_6H_4]Se–S–PMe_2=N–PPh_2=S (**8**). Attempts to prepare the analogous [2-(Me_2NCH_2)-C_6H_4]Se–S–PPh_2=N–PPh_2=S (**9**) by metathesis reaction between **3** and K[$(SPPh_2)_2N$] always resulted in an impure yellow solid containing traces of the free dithioligand, $(SPPh_2)_2NH$ (see Section 2.2), which indicates that the compound is quite sensitive to hydrolysis.

Compounds **2**–**8** can be recrystallized from CH_2Cl_2/*n*-hexane mixtures as stable, yellow, crystalline solids (except compound **4**, whose crystals are red). The trichloride **5** decomposes slowly in $CDCl_3$ solution to the monochloride **2** and elemental chlorine, as indicated by NMR spectra.



Scheme 1.

2.2. NMR spectra

The room-temperature NMR (^{1}H, ^{13}C) spectra of compounds **2**–**8** in $CDCl_3$ solution are very similar with respect to the organic ligand attached to selenium, showing the expected resonances in the alkyl and the aryl region (the assignment of the signals was based on 2D experiments). In all cases the resonances for the protons of the pendant CH_2NMe_2 arm appear as singlets in the region 2.30–3.00 ppm for CH_3 and 3.60–4.50 ppm for CH_2, respectively (cf. $PhCH_2NMe_2$ [20]: δ 2.24 and 3.40 ppm, respectively). This is consistent either with (i) the absence of an intramolecular Se···N interaction; (ii) a fast process involving several steps – dissociation–regeneration of the internal Se···N interaction, with pyramidal inversion at the nitrogen center, as proposed for analogous [2-(CyMeNCH$_2$)C$_6$H$_4$]SeX derivatives [23]; or (iii) a fast conformational change of the chelate five-membered SeC_3N ring [assuming a planar (C,N)SeX core] in solution, thus yielding averaged NMR resonances. The spectra of compound **4** (^{1}H) and compound **6** (^{1}H, ^{13}C) remained unchanged when recorded in DMSO-d_6 solutions, so that no conclusion concerning possible Se···N interaction could be drawn.

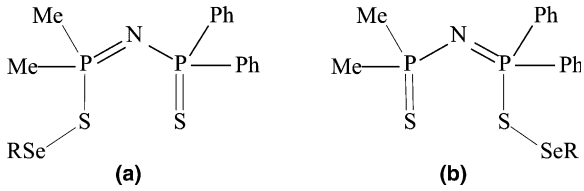
The reported ^{77}Se chemical shifts in $CDCl_3$ solution for [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeX (δ 1030, 987 and 818 ppm for X = Cl [17], Br and I [20]) are of the same magnitude as those found for [2-(CyMeNCH$_2$)C$_6$H$_4$]SeX derivatives (δ 1051 and 1011 ppm for X = Cl and Br, respectively) [23], for which the presence of the internal Se···N interaction in solution was well documented by multinuclear NMR studies. Therefore, it might be concluded that such an internal Se···N interaction is also present in solution for compounds **2**–**4**. It should be noted that the ^{77}Se resonances of the RSeX derivatives [R = 2-(4,4-dimethyl-2-oxazolinyl)phenyl], which are also stabilized by an internal Se···N interaction [29], are strongly upfield shifted (δ 855.9, 849.5, and 762.2 ppm for X = Cl, Br and I, respectively) compared to those of [2-(Me$_2$NCH$_2$)-C$_6$H$_4$]SeX, although they follow the same trend with respect to the electronegativity of the halogen. This behavior indicates that, in addition to the effect of the halogen atom, the nature of the organic group attached to selenium can exhibit a considerable effect on the magnitude of the ^{77}Se chemical shifts and this effect should be considered when comparisons are made between NMR parameters observed for different series of compounds.

The increase in the oxidation state of the selenium atom in [2-(Me$_2$NCH$_2$)C$_6$H$_4$]SeCl$_3$ (**5**) is reflected in downfield shifts of ^{1}H resonances for all types of protons in comparison with **2**. In the ^{13}C spectrum of **5** a larger deshielding was observed for the C_1 atom directly attached to selenium (δ 148.72 ppm in **5** vs. 138.06 ppm for **2**), in agreement with the increase of electronegativity with the number of chlorine atoms attached to the chalcogen.

In addition to the resonances for the organic ligand attached to selenium, the ^{1}H and ^{13}C NMR spectra for compounds **6** and **7** exhibit signals for nonequivalent organic groups in the diorganodithiocarbamato moiety. This behavior is consistent with the partial double bond nature of the carbon–nitrogen bond and the monodentate coordination pattern of the dithioligand in solution.

The dichalcogenoimidodiphosphinato ligands of type $[(XPR_2)(YPR'_2)N]^-$ (X, Y = O, S, Se), are well known versatile ligands able to adjust to various coordination geometries required by metal centers [30]. Compared with the restrictive "bites" in 1,1-dichalcogenophosphorus ligands (e.g. dithiophosphates, $[(RO)_2PS_2]^-$, dithiophosphinates, $[R_2PS_2]^-$, or dithiocarbamates, $[R_2NCS_2]^-$), the flexibility of the XPNPY skeleton allows for a considerably wider range of "bite" so that such ligands are particularly appropriate for the investigation of the competition for internal coordination to the selenium center when different donor atoms are available. The ^{31}P spectrum (in $CDCl_3$) of the solid product (**9**) isolated from there action of **3** with K[(SPPh$_2$)$_2$N] exhibits two broad, singlet resonances in a 1:1 intensity ratio (the sample was always contaminated with some free dithio acid, resulting in a residual ^{31}P signal at δ 58.3 ppm; cf. (SPPh$_2$)$_2$NH [31]: δ 57.6 ppm). This is consistent with monodentate coordination of the ligand through only one of the sulfur atoms to selenium and the formulation of compound **9** as [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Se–S–PPh$_2$=N–PPh$_2$=S with the two ^{31}P resonances assigned to Ph$_2$*P*–S (δ 30.9 ppm) and Ph$_2$*P*=S (δ 43.6 ppm), respectively (cf. MeS–PPh$_2$=N–PPh$_2$=S [32]: δ 30.9 (Ph$_2$*P*–S), 42.0 ppm (Ph$_2$*P*=S)). The solution behaviour of **9** is similar to that found for the tellurium analogue, [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Te–S–PPh$_2$=N–PPh$_2$=S [δ 31.7 (Ph$_2$*P*–S), 41.9 ppm (Ph$_2$*P*=S)], for which the molecular structure and the monodentate pattern of the dithioligand in the solid state were also established by single-crystal X-ray diffraction [33].

When an asymmetric dithioimidodiphosphinato ligand is present as in the case of compound **8**, two isomers are possible, i.e. (**a**) or (**b**). The ^{1}H and ^{13}C NMR spectra of **8** ($CDCl_3$ solution) exhibit the resonances for the organic groups attached to the phosphorus atom, with the splitting pattern due to phosphorus–proton and phosphorus–carbon couplings, as expected for only one isomer. The ^{31}P spectrum contains two resonances which were assigned to Me$_2$*P*-S (δ 40.8 ppm, d, $^3J_{PP}$ 8.3, $^1J_{PC}$ 71.1 Hz) and Ph$_2$*P*=S (δ 42.6 ppm, d, $^3J_{PP}$ 8.3, $^1J_{PC}$ 107.7 Hz) on the basis of the $^1J_{PC}$ coupling constants, thus being consistent with the presence of isomer (**a**) in solution.



The ^{77}Se NMR spectra of organoselenium(II) derivatives containing dithioligands contain only one resonance thus indicating the presence of only one Se-containing species in solution. The magnitude of the ^{77}Se chemical shifts, i.e. δ 631.9 (**6**) and 579.9 ppm (**8**), are similar to those observed for thiophenolato derivatives [2-(Me_2NCH_2)C_6H_4]SeSPh (δ 562.3 ppm, in 1:1 CD_3OH–$CDCl_3$) [15] or [2-($CyMeNCH_2$)C_6H_4]SeSPh (δ 571.5 ppm, in $CDCl_3$) [21]. The upfield shifts observed for the thio derivatives **6**–**8** in comparison with the halides **2**–**4** are consistent with a decreased deshielding as the electronegativity of the substituent on the Se atom decreases [34].

2.3. Crystal and molecular structure of [2-(Me_2NCH_2)-C_6H_4]SeX [X = Cl (**2**), I (**4**)] and [2-(Me_2NCH_2)-C_6H_4]$SeCl_3$ (**5**)

Single crystals suitable for X-ray diffraction studies were obtained from CH_2Cl_2/*n*-hexane for the halides **2**, **4**, and **5**. Selected interatomic distances and angles are listed in Table 1. It was shown previously that intramolecular coordination of the nitrogen atom to a metal center in compounds containing a [2-(Me_2NCH_2)-C_6H_4]M moiety induces chirality at the metal center [35–38]. Indeed, the crystals of compounds **2**, **4**, and **5** contain 1:1 mixtures of *R*- and *S*-isomers [with the C(1)–C(6) aromatic ring and the N(1) atom as chiral plane and pilot atom, respectively] [39]. The ORTEP diagrams for the (*S*)-**2** and (*R*)-**4** isomers are shown in Fig. 1(a) and (b), while an ORTEP representation of the dimer association found in the crystal of **5** (see subsequent discussion) is depicted in Fig. 1(c).

Table 1
Selected interatomic distances (Å) and angles (°) in **2**, **4** and **5**

	2 (X = Cl)	**4** (X = I)	**5** (X = Cl)
Se(1)–C(1)	1.926(2)	1.930(3)	1.937(3)
Se(1)–N(1)	2.137(2)	2.167(3)	2.276(2)
Se(1)–X(1)	2.4757(7)	2.8227(4)	2.3459(9)
Se(1)–Cl(2)			2.3610(9)
Se(1)–Cl(3)			2.4349(9)
N(1)–C(7)	1.480(3)	1.484(4)	1.479(4)
N(1)–C(8)	1.478(3)	1.477(4)	1.481(4)
N(1)–C(9)	1.479(3)	1.479(4)	1.481(3)
N(1)–Se(1)–X(1)	175.97(5)	179.03(7)	174.71(6)
Cl(2)–Se(1)–Cl(3)			177.40(3)
C(1)–Se(1)–N(1)	81.47(8)	81.6(1)	80.1(1)
C(1)–Se(1)–X(1)	94.59(7)	97.53(9)	95.83(9)
C(1)–Se(1)–Cl(2)			91.55(8)
C(1)–Se(1)–Cl(3)			90.42(8)
N(1)–Se(1)–Cl(2)			93.40(6)
N(1)–Se(1)–Cl(3)			88.62(6)
Cl(1)–Se(1)–Cl(2)			90.02(4)
Cl(1)–Se(1)–Cl(3)			88.08(4)
C(7)–N(1)–C(8)	112.0(2)	111.4(3)	109.7(2)
C(7)–N(1)–C(9)	111.7(2)	112.2(3)	113.3(2)
C(8)–N(1)–C(9)	111.0(2)	111.4(3)	109.9(2)
Se(1)–N(1)–C(7)	103.2(1)	103.4(2)	102.4(2)
Se(1)–N(1)–C(8)	109.1(2)	109.6(2)	113.8(2)
Se(1)–N(1)–C(9)	109.5(1)	108.4(2)	107.7(2)

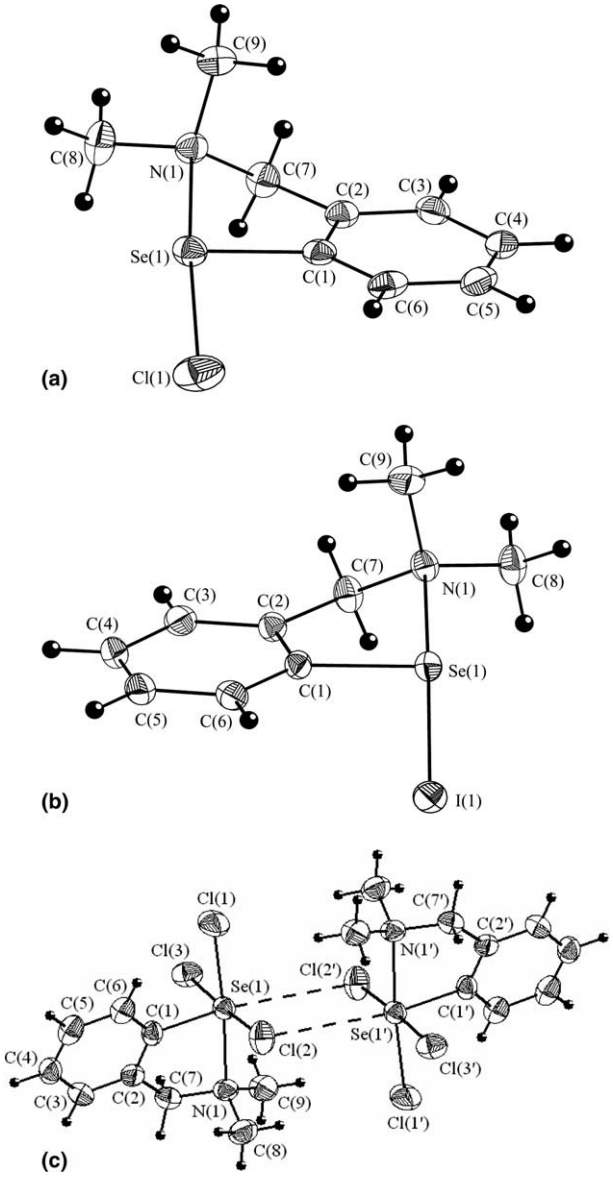


Fig. 1. ORTEP representation at 50% probability and atom numbering scheme for (a) the (*S*)-**2** isomer; (b) the (*R*)-**4** isomer; and (c) the dimer association of (*R*)/(*S*) isomers in the crystal of **5** [symmetry equivalent atoms ($1-x$, $2-y$, $2-z$) are given by "prime"].

For all three halides, the 2-(Me_2NCH_2)C_6H_4 moiety acts as a (*C*,*N*)-ligand with the nitrogen atom very strongly coordinated to the selenium centre *trans* to a Se–halogen bond (cf. the sums of the covalent and van der Waals radii are $\sum_{cov}$(Se,N) ca. 1.87 Å and $\sum_{vdW}$(Se,N) ca. 3.54 Å [40]). This results in a T-shaped (*C*,*N*)SeX core (hypervalent 10-Se-3 species [41]) for compounds **2** and **4** [N(1)–Se(1)–X(1) 175.97(5) and 179.03(7)°, respectively]. The decrease in the electronegativity of the halogen in the [2-(Me_2NCH_2)C_6H_4]SeX series does not strongly affect the strength of the internal Se···N interaction [Se(1)–N(1) 2.137(2) (cf. 2.135(4) [17]), 2.143(6) [20] and 2.167(3) (cf. 2.172(3) [17]) Å for **2**, **3**, and **4**], as was more evident in the [2-(4,4-dimethyl-2-oxazolinyl)phenyl]SeX series [Se–N 2.052(2), 2.063(3) and 2.133(4) Å for X = Cl, Br and I] [29]. The linear arrangement of the N···Se–X unit (3c–4e system) results in the elongation of the Se–halogen bonds in organoSe(II) halides stabilized by internal Se···N interaction. The Se–halogen bond lengths [Se(1)–X(1) 2.4757(7) Å (cf. 2.471(2) [17]), 2.634(1) [20] and 2.8227(4) (cf. 2.8079(7) [17]) Å in in **2**, **3**, and **4**] are similar to those found in the related [8-$Me_2NC_{10}H_6$]SeX [Se–X 2.429(2) and 2.7419(9) for X = Cl and I] [42] or [2-(4,4-dimethyl-2-oxazolinyl)phenyl]SeX [Se–X 2.482(8), 2.6318(7) and 2.7773(7) Å for X = Cl, Br and I] [29]. They are considerably longer than observed for [2,4,6-$Me_3C_6H_2$]SeX [Se–X 2.186(1), 2.3331(8) and 2.529(1) Å for X = Cl, Br [43] and I [44]].

In the crystals of **2** and **4** the molecular units are separated by normal van der Waals distances between heavy atoms [longer than the sums of the respective van der Waals radii $\sum_{vdW}$(Se,Cl) ca. 3.80 Å, $\sum_{vdW}$(Se,I) ca. 4.15 Å [40]]. This is in contrast to the [2-(4,4-dimethyl-2-oxazolinyl)phenyl]SeX derivatives, the molecules of which were found to form dimer associations in the crystal, through weak intermolecular Se···X interactions [3.476(8), 3.556(9) and 3.752(2) Å for X = Cl, Br, I] [29]. A closer check of the crystal structures of **2** and **4** revealed several hydrogen bonding interactions resulting in similar supramolecular arhitectures. Within a molecule of [2-(Me_2NCH_2)C_6H_4]SeX there is a short intramolecular X···H contact: Cl(1)···H(6) 2.73 Å and I(1)···H(6) 2.95 Å [cf. sum of the respective van der Waals radii is $\sum_{vdW}$(Cl,H) ca. 3.0 Å and $\sum_{vdW}$(I,H) ca. 3.35 Å] [40]. Dimer associations are formed between pairs of *R*- and *S*-isomers through intermolecular X···H_{methyl} contacts [Cl(1)···H(8B′) 2.82 Å and I(1)···H(8A′) 3.20 Å] (Fig. 2(a)). Further inter-dimer X···$H_{methylene}$ contacts [Cl(1)···H(7B′c) 2.88 Å and I(1)···H(7B′c) 3.22 Å] led to a layered structure in which a dimer unit is connected to four neighboring dimers (Fig. 2(b)). For compound **4** additional weak interdimer I···H_{methyl} contacts are established [I(1)···H(9C′d) 3.18 Å].

The Se(1)–N(1) distance in the trichloride **5** is surprisingly slightly longer [2.276(2) Å] than in **2**, but still corresponds to a strong interaction. The Se–Cl bond

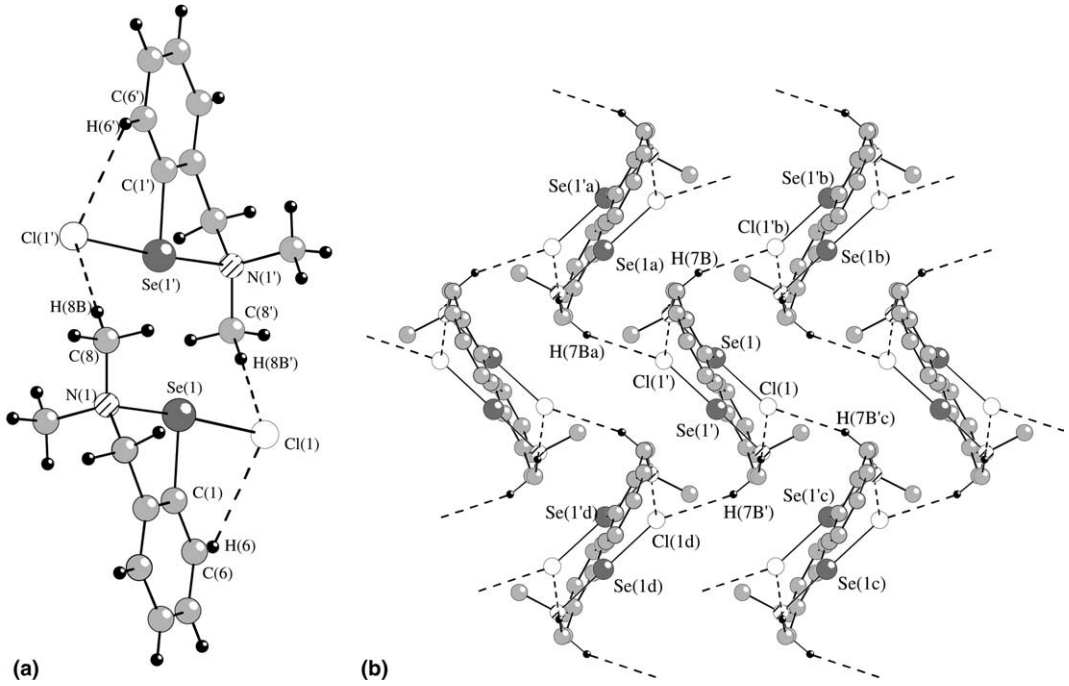


Fig. 2. Hydrogen bonding in the crystal of **2**: (a) dimer association of (*R*)-**2**/(*S*)-**2** isomers [symmetry equivalent atoms ($-x$, $-y$, $-z$) are given by "prime"]; and (b) view along *c* axis of a layer network based on intermolecular hydrogen bonding [only hydrogens involved in intermolecular interactions are shown; 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 ($-0.5 + x$, $-0.5 - y$, $-z$) are given by "a", "prime b", "prime c" and "d"].

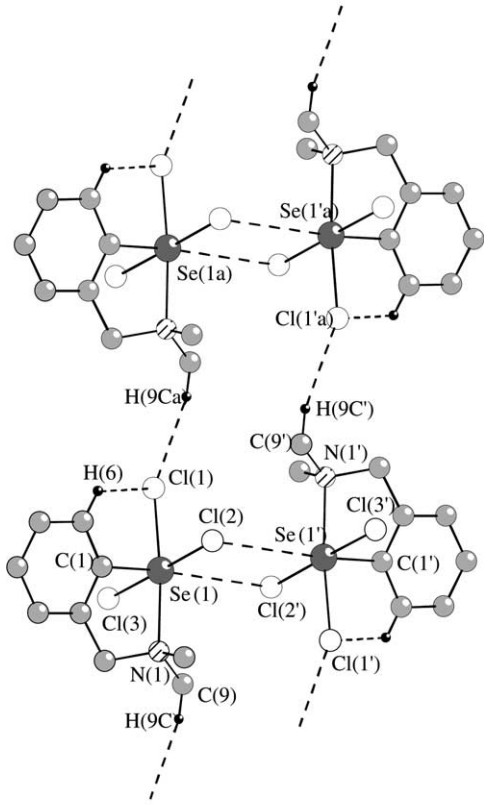


Fig. 3. View of the polymeric association of dimers based on intermolecular hydrogen bonding in the crystal of **5** [only hydrogens involved in Cl···H contacts are shown; symmetry equivalent atoms $(-1+x,\ 1+y,\ z)$ and $(-1+x,\ 3-y,\ 2-z)$ are given by "a" and "prime a"].

distances are shorter than in **2** and are different (Table 1), the shorter one corresponding to the Cl(1) atom *trans* to the nitrogen. The coordination geometry around the Se center is distorted square pyramidal, with the aromatic *ipso* carbon in apical position [N(1)–Se(1)–Cl(1) 174.71(6)°, Cl(2)–Se(1)–Cl(3) 177.40(3)°]. Dimer associations between pairs of *R*- and *S*-isomers are formed through weak intermolecular Se···Cl interactions [Se(1)–Cl(2′) 3.400(4) Å] *trans* to the Se(1)–C(1) bond [Cl(2′)···Se(1)–C(1) 171.0(1)°], with the internal Se–N interactions placed in *trans* with respect to the planar Se_2Cl_2 ring thus formed (Fig. 1(c)). The overall coordination geometry around selenium can be described as distorted octahedral [(*C*,*N*)$SeCl_4$ core, hypervalent 14-Se-6 species [41]]. Similar dimer associations based on much stronger intermolecular Se···Cl interactions are found in the crystals of CF_3SeCl_3 [folded Se_2Cl_2 ring (folding angle 154°), bridging Se–Cl distances in the range 2.51(2)–2.75(2) Å and *cis* Se–C bonds] [25] and 3,5-Pr^i_2-4-$(Me_3Si)_2N$–$C_6H_2SeCl_3$ [planar Se_2Cl_2 ring, bridging Se–Cl distances 2.587(2)–2.749(2) Å and *trans* Se–C bonds] [27]. In addition to the intramolecular Cl(1)···H(6) interaction [2.66 Å], in the crystal of **5** there are short inter-dimer $Cl\cdots H_{methyl}$ contacts [Cl(1)···H(9Ca) 2.74 Å] which result in a columnar polymeric association of the dimers (Fig. 3).

Table 2
Selected interatomic distances (Å) and angles (°) in **6**, **7** and **8**

	6	**7**	**8**
Se(1)–C(1)	1.929(2)	1.941(5)	1.942(3)
Se(1)–N(1)	2.443(2)	2.472(4)	2.439(3)
Se(1)–S(1)	2.2659(7)	2.247(1)	2.291(1)
N(1)–C(7)	1.455(3)	1.461(6)	1.442(5)
N(1)–C(8)	1.451(3)	1.449(6)	1.444(5)
N(1)–C(9)	1.469(3)	1.475(6)	1.458(6)
C(10)–S(1)	1.783(2)	1.797(5)	
C(10)–S(2)	1.660(2)	1.659(5)	
C(10)–N(2)	1.330(3)	1.342(6)	
C(11)–N(2)	1.467(4)	1.470(6)	
C(X)–N(2)[a]	1.462(3)	1.470(6)	
P(1)–S(1)			2.088(1)
N(2)–P(1)			1.567(3)
N(2)–P(2)			1.614(3)
P(2)–S(2)			1.964(1)
C(1)–Se(1)–N(1)	78.78(8)	77.0(2)	78.0(1)
C(1)–Se(1)–S(1)	100.17(7)	99.0(2)	96.6(1)
N(1)–Se(1)–S(1)	175.69(5)	173.3(1)	172.5(1)
Se(1)–S(1)–C(10)	106.46(8)	106.8(2)	
S(1)–C(10)–S(2)	122.1(1)	122.2(3)	
N(2)–C(10)–S(1)	113.8(2)	113.4(3)	
N(2)–C(10)–S(2)	124.1(2)	124.4(4)	
C(10)–N(2)–C(11)	120.8(2)	124.4(4)	
C(10)–N(2)–C(X)	123.8(2)	120.2(4)	
C(11)–N(2)–C(X)	115.4(2)	115.4(4)	
C(7)–N(1)–C(8)	111.8(2)	112.7(4)	113.1(4)
C(7)–N(1)–C(9)	113.5(2)	111.4(4)	111.7(4)
C(8)–N(1)–C(9)	111.9(2)	111.7(4)	111.2(4)
Se(1)–N(1)–C(7)	100.8(1)	98.6(3)	97.5(2)
Se(1)–N(1)–C(8)	110.7(2)	108.7(3)	115.0(3)
Se(1)–N(1)–C(9)	107.4(2)	113.1(3)	107.6(3)
Se(1)–S(1)–P(1)			98.65(4)
S(1)–P(1)–N(2)			115.1(1)
P(1)–N(2)–P(2)			137.1(2)
S(2)–P(2)–N(2)			120.3(1)

[a] C(X) = C(12) and C(13) for **6** and **7**, respectively.

*2.4. Crystal and molecular structure of [2-(Me_2NCH_2)-C_6H_4]SeS(S)CNR_2 [R = Me (**6**), Et (**7**)] and [2-(Me_2NCH_2)C_6H_4]Se–S–PMe_2═N–PPh_2═S (**8**)*

Single crystals suitable for X-ray diffraction studies were obtained from CH_2Cl_2/*n*-hexane for compounds **6**–**8** which contain a dithioligand. Selected interatomic distances and angles are listed in Table 2. The crystals of compounds **6** and **8** contain 1:1 mixtures of *R*- and *S*-isomers, while for **7** the crystal contains only the isomer *R*. The ORTEP diagrams for the (*S*)-**6**, (*R*)-**7** and (*R*)-**8** isomers are shown in Fig. 4.

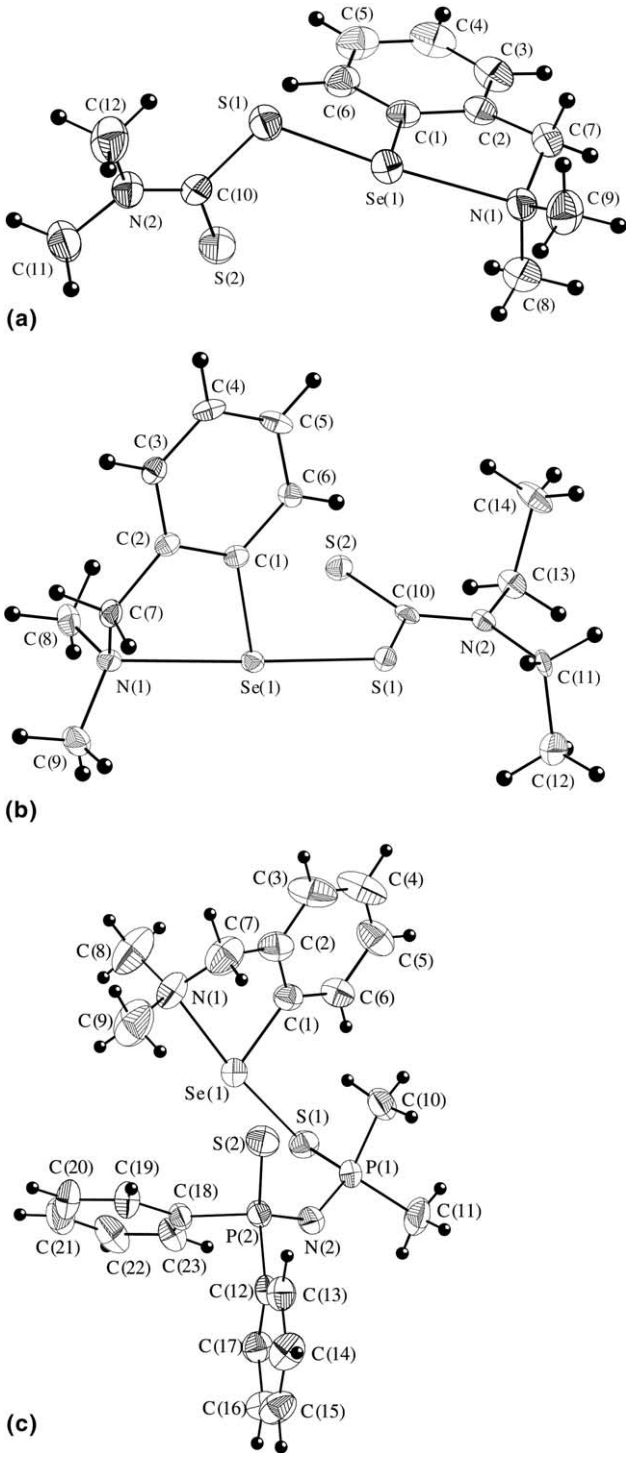


Fig. 4. ORTEP representation at 40% probability and atom numbering scheme for (a) the (*S*)-**6**; (b) the (*R*)-**7**; and (c) the (*R*)-**8**-isomers.

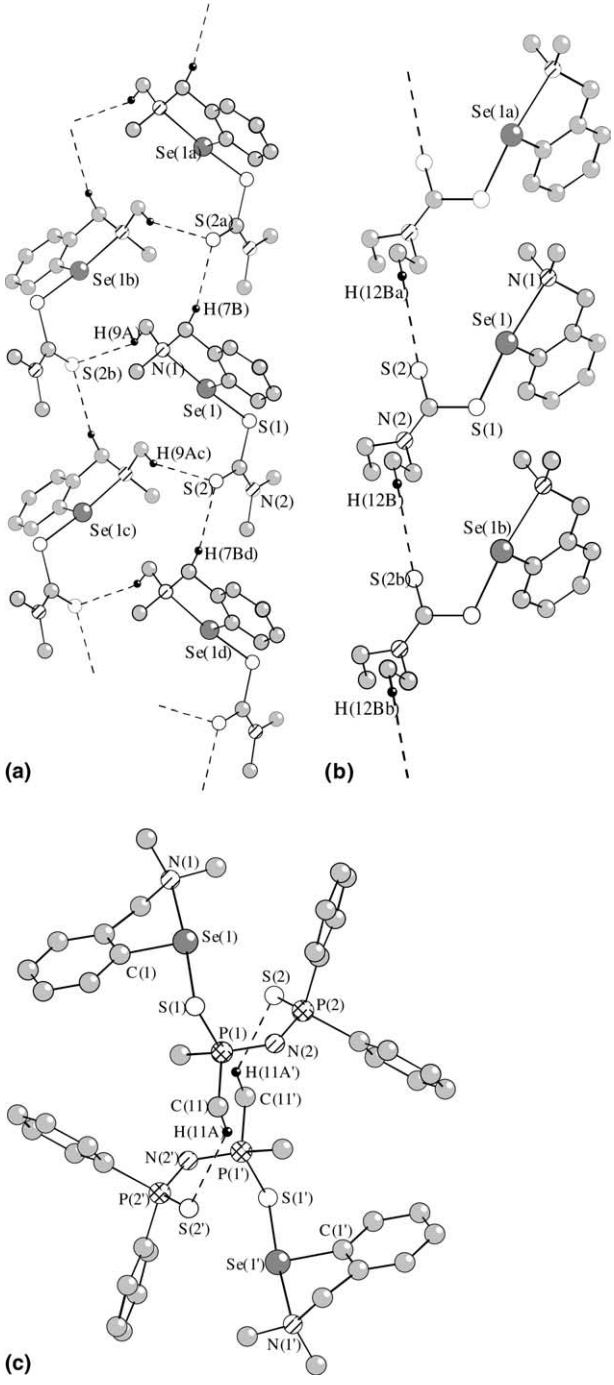


Fig. 5. Associations in the crystals of compounds **6**–**8** based on S···H contacts (only hydrogens involved in such contacts are shown): (a) double-chain polymer of (*S*)-**6** isomers [symmetry equivalent atoms (x, $1+y$, z), ($-0.5+x$, $0.5+y$, $0.5-z$), ($-0.5+x$, $-0.5+y$, $0.5-z$) and (x, $-1+y$, z) are given by "a", "b", "c" and "d"]; (b) single-chain polymer of (*R*)-**7** isomers [symmetry equivalent atoms ($1+x$, y, z) and ($-1+x$, y, z) are given by "a" and "b"]; and (c) dimer association of (*R*)/(*S*)-**8** isomers [symmetry equivalent atoms ($-x$, $-y$, $1-z$) are given by "prime"].

As in the case of halides **2** and **4** described above, the molecules of compounds **6**–**8** feature a T-shaped coordination environment of the selenium center [(*C*,*N*)SeS core] due to an internal Se···N interaction *trans* to a sulfur atom [Se(1)–N(1)/N(1)–Se(1)–S(1) 2.4433(19) Å/175.69(5)°, 2.472(4) Å/173.3(1)° and 2.439(3) Å/172.47(8)° for **6**, **7**, and **8**, respectively]. The increase of the Se–N distances in the thio derivatives **6**–**8** reflects the decreased electronegativity of the sulfur atom in

comparison to that of the halogens in **2** and **4**. Internal Se···N interactions of intermediate strengths were observed in the [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 derivatives [2.359(2) Å and 2.397(2) Å for R = Ph and OPr^i, respectively] [28].

Regardless of the magnitude of their "bite" size, the dithioligands act as monodentate moieties in all three of these compounds, being attached to the Se center through only one sulfur atom. The Se(1)–S(1) bond distances [2.2659(7), 2.247(1) and 2.2911(10) Å for **6**, **7**, and **8**] are within the expected range for covalent selenium–sulfur single bonds, but are stronger than those observed for related [2-(Me_2NCH_2)C_6H_4]SeS(S)PR_2 derivatives [2.3400(7) Å and 2.3373(10) Å for R = Ph and OPr^i, respectively] [28]. The second sulfur atom of the dithioligands is not involved in any intermolecular interaction with selenium atoms. However, due to the smaller "bite" of the dithiocarbamato moiety the S(2) atom is brought closer to the selenium center [Se(1)···S(2) 3.483(1) in **6**, and 3.433(1) Å in **7**] than in the dithioimidodiphosphinato derivative **8** [Se(1)···S(2) 4.430(1) Å; cf. the sums of the covalent and van der Waals radii are $\sum_{cov}$(Se,S) ca. 2.21 Å and $\sum_{vdW}$(Se,S) ca. 3.85 Å [40]]. The monodentate nature of the dithioligands in compounds **6**–**8** is also supported by the differences in the carbon–sulfur bond lengths within a dithiocarbamato moiety and the phosphorus–sulfur and phosphorus–nitrogen bond lengths in **8** (Table 2) [cf. MeS–PPh_2═N–PPh_2═S [32]: P–S 2.071(1) Å, P═S 1.954(1) Å, P–N 1.610(2) Å, P═N 1.562(2) Å].

A short intramolecular S(1)···H(6) contact, analogous to the Cl(1)···H(6) one observed for the halide species **2** and **4**, is also present within the molecules of the dithio derivatives **6**–**8** (2.73, 2.76, and 2.70 Å for **6**, **7**, and **8**, respectively; cf. sum of the van der Waals radii is $\sum_{vdW}$(S,H) ca. 3.05 Å [40]). The crystals of compounds **6**–**8** also feature associations of the molecular units through weak intermolecular S···H contacts. The change in the nature of the organic group of the dithiocarbamato moiety results in different chain polymeric associations for **6** and **7**. In the crystal of **6** there are parallel chains along the *b* axis built from *R*- and *S*-isomers, respectively, through S···$H_{methylene}$ contacts [S(2)···H(7Bd) 2.92 Å]. Inter-chain S···$H_{N\text{-}methyl}$ contacts [S(2)···H(9Ac) 2.96 Å] result in pairs of (*R*,*R*) and (*S*,*S*) chains (Fig. 5(a)). In contrast to **6**, in the case of **7**, a methyl proton of an ethyl group is involved in the S···H contact [S(2)···H(12Ba) 3.00 Å] which results in chains built from *R*-isomers; there are no further interchain S···H contacts shorter than the corresponding sum of the van der Waals radii (Fig. 5(b)).

Discrete dimer associations are present in the crystal of **8**. They are formed between pairs of *R*- and *S*-isomers through intermolecular S···$H_{P\text{-}methyl}$ contacts [S(2)···H(11A′) 2.93 Å] (Fig. 5(c)).

3. Conclusions

New organoselenium(II) compounds containing the 2-(Me_2NCH_2)C_6H_4 moiety were prepared and their hypervalent nature was investigated both in solution and in solid state. The molecular structure of the new organoselenium(IV) trihalide [2-(Me_2NCH_2)C_6H_4]$SeCl_3$ was also established by X-ray diffraction. The dithioligands in [2-(Me_2NCH_2)C_6H_4]SeS(S)CNR_2 [R = Me, Et] and [2-(Me_2NCH_2)C_6H_4]Se–S–PMe_2═N–PPh_2═S were found to act as monodentate units in both solution and the solid state. In the solid state, compounds **2**, **4**–**6**, and **8** crystallize as 1:1 mixtures of *R*- and *S*-isomers, while for **7** the crystal contains only the isomer *R*. In the crystals, a network of intermolecular X···H contacts (X = Cl, I, S) generates different supramolecular architectures, i.e. discrete dimers, polymeric chains or layer structures.

4. Experimental

4.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled prior to use. Selenium, *N*,*N*-dimethylbenzylamine, butyllithium (15% in hexane), Na[S_2CNMe_2]·$2H_2O$ and Na[S_2CNEt_2]·$3H_2O$ were commercially available. The other starting materials were prepared according to the literature methods: [2-(Me_2NCH_2)C_6H_4]Li [45], [2-(Me_2NCH_2)C_6H_4]$_2Se_2$ (**1**) [20] and K[($SPMe_2$)($SPPh_2$)N] [46]. Room-temperature ^1H and ^{13}C NMR spectra for compounds **3**–**7** (in dried $CDCl_3$), including 2D experiments, were recorded on a BRUKER AVANCE DRX 400 instrument operating at 400.2 and 100.6 MHz, respectively. The ^1H and ^{13}C NMR spectra for **2** and **8** (in dried $CDCl_3$) and **4** and **6** (in DMSO-d_6), as well as ^{31}P NMR spectrum of **8** were recorded at room temperature on a VARIAN GEMINI 300S instrument operating at 299.5, 75.4 and 121.4 MHz, respectively. The chemical shifts are reported in ppm relative to the residual peak of solvent (ref. $CHCl_3$: ^1H 7.26, ^{13}C 77.0 ppm; DMSO-d_6: ^1H 2.50, ^{13}C 39.43 ppm) and H_3PO_4 85%, respectively. The ^{77}Se spectra were obtained at 57.2 MHz, in $CDCl_3$ on a VARIAN MERCURY 300BB spectrometer using diphenyl diselenide (80 °C) as external standards. Chemical shifts are reported relative to dimethyl selenide (^{77}Se) (0 ppm) by assuming that the resonance of the standard is at 460 ppm [47]. Abbreviations used in multiplicities are: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; t, triplet; q, quartet; m, multiplet.

4.2. Preparation of [2-(dimethylaminomethyl)phenyl]-selenium(II) chloride, [2-(Me_2NCH_2)C_6H_4]SeCl (**2**)

A solution of **1** (0.85 g, 2.0 mmol) in 50 ml carbon tetrachloride was treated dropwise with a solution of sulfurylchloride (0.27 g, 2.0 mmol) in 40 ml carbon tetrachloride. The reaction mixture was stirred at room temperature for additional 2 h, then the resulting solid was filtered off and washed with hexane. It was recrystallized from CH_2Cl_2/*n*-hexane (1:5, v/v) to give **2** as pale yellow crystals. Yield: 0.7 g (71%). M.p. 111–113 °C (lit. 118–121 °C, dec. [17]). ^{1}H NMR: δ 2.79s (6H, N–CH_3), 4.02s (2H, –CH_2–), 7.13d (1H, H_3, $^3J_{HH}$ 7.2 Hz), 7.19dd (1H, H_4, $^3J_{HH}$ 7.2, $^3J_{HH}$ 7.2 Hz), 7.33dd (1H, H_5, $^3J_{HH}$ 7.4, $^3J_{HH}$ 7.4 Hz), 8.11d (1H, H_6, $^3J_{HH}$ 7.9 Hz). ^{13}C NMR: δ 47.29 (N–CH$_3$), 66.16 (–CH$_2$–), 125.09 (C_3), 126.20 (C_4), 129.16, 129.20 ($C_{5,6}$), 134.16 (C_2), 138.06 (C_1).

4.3. Preparation of [2-(dimethylaminomethyl)phenyl]-selenium(II) bromide, [2-(Me_2NCH_2)C_6H_4]SeBr (**3**)

Prepared and worked up as for compound **2**, from **1** (1.00 g, 2.34 mmol) and Br_2 (0.37 g, 2.34 mmol) in carbon tetrachloride. Yield: 1.12 g (81%). M.p. 149 °C (lit. 149 °C, dec. [20]). ^{1}H NMR: δ 2.76s (6H, N–CH_3), 3.97s (2H, –CH_2–), 7.09d (1H, H_3, $^3J_{HH}$ 7.4 Hz), 7.19dd (1H, H_4, $^3J_{HH}$ 7.4, $^3J_{HH}$ 7.4 Hz), 7.30dd (1H, H_5, $^3J_{HH}$ 7.4, $^3J_{HH}$ 7.4 Hz), 8.13d (1H, H_6, $^3J_{HH}$ 8.0 Hz). ^{13}C NMR: δ 47.05 (N–CH$_3$), 66.00 (–CH$_2$–), 125.23 (C_3), 126.34 (C_4), 129.20 (C_5), 131.26 (C_6), 134.69 (C_2), 135.92 (C_1).

4.4. Preparation of [2-(dimethylaminomethyl)phenyl]-selenium(II) iodide, [2-(Me_2NCH_2)C_6H_4]SeI (**4**)

Prepared and worked up as for compound **2**, from **1** (0.62 g, 1.4 mmol) and I_2 (0.37 g, 1.4 mmol) in carbon tetrachloride. Yield: 0.8 g (81%). M.p. 148 °C (lit. 152 °C [20]). ^{1}H NMR ($CDCl_3$): δ 2.63s (6H, N–CH_3), 3.79s (2H, –CH_2–), 7.03d (1H, H_3, $^3J_{HH}$ 6.9 Hz), 7.23m (2H, $H_{4,5}$), 8.07d (1H, H_6, $^3J_{HH}$ 8.0 Hz). ^{1}H NMR (DMSO-d_6): δ 2.80s (6H, N–CH_3), 4.12s (2H, –CH_2–), 7.28m (3H, $H_{3\text{-}5}$), 7.95m (1H, H_6). ^{13}C NMR ($CDCl_3$): δ 46.06 (N–CH$_3$), 66.24 (–CH$_2$–), 125.63 (C_3), 126.40 (C_4), 129.15 (C_5), 131.95 (C_1), 135.46 (C_6), 136.12 (C_2).

4.5. Preparation of [2-(dimethylaminomethyl)phenyl]-selenium(IV) trichloride, [2-(Me_2NCH_2)C_6H_4]$SeCl_3$ (**5**)

A solution of **1** (0.33 g, 0.77 mmol) in 50 ml carbon tetrachloride was treated dropwise with a solution of sulfurylchloride (0.31 g, 2.34 mmol) in 40 ml carbon tetrachloride. The reaction mixture was stirred at room temperature for 2 h and the deposited solid was filtered off and washed with hexane. Its recrystallization from CH_2Cl_2/*n*-hexane (1:5, v/v) gave **5** as yellow crystals. Yield: 0.44 g (89%). M.p. 120–122 °C. Anal. Found: C, 33.54; H, 3.62; N, 4.12. Calc. for $C_9H_{12}Cl_3NSe$: C, 33.83; H, 3.79; N, 4.38%. ^{1}H NMR: δ 2.99s (6H, N–CH_3), 4.49s (2H, –CH_2–), 7.31d (1H, H_3, $^3J_{HH}$ 7.3 Hz), 7.53dd (1H, H_4, $^3J_{HH}$ 7.5, $^3J_{HH}$ 7.5 Hz), 7.59dd (1H, H_5, $^3J_{HH}$ 7.5, $^3J_{HH}$ 7.9 Hz), 8.57d (1H, H_6, $^3J_{HH}$ 8.1 Hz). ^{13}C NMR: δ 48.20 (N–CH$_3$), 63.96 (–CH$_2$–), 126.83 (C_3), 128.90 (C_6), 130.59 (C_5), 132.10 (C_4), 137.22 (C_2), 148.72 (C_1).

4.6. Preparation of [2-(dimethylaminomethyl)phenyl]-selenium(II) dimethyldithiocarbamate, [2-(Me_2NCH_2)-C_6H_4]SeS(S)$CNMe_2$ (**6**)

A mixture of **3** (0.44 g, 1.5 mmol) and Na[S_2CN-Me_2] · 2H_2O (0.26 g, 1.45 mmol) in 25 ml anhydrous CH_2Cl_2 was stirred at room temperature for 12 h. The reaction mixture was filtered to remove NaBr and the clear yellow filtrate was concentrated in vacuo until a yellow solid deposited. The solid was filtered off and recrystallization from CH_2Cl_2/*n*-hexane (1:5, v/v) affords yellow crystals of **6**. Yield: 0.3 g (62%). M.p. 76–78 °C. Anal. Found: C, 42.94; H, 5.27; N, 8.23. Calc. for $C_{12}H_{18}N_2S_2Se$: C, 43.24; H, 5.44; N, 8.40%. ^{1}H NMR ($CDCl_3$): δ 2.39s (6H, N–CH_3), 3.55s [3H, (S_2C)N–CH_3 (A)], 3.63s [3H, (S_2C)N–CH_3 (B)], 3.67s (2H, –CH_2–), 7.10m (2H, $H_{3,4}$), 7.18ddd (1H, H_5, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.3, $^4J_{HH}$ 2.0 Hz), 7.69d (1H, H_6, $^3J_{HH}$ 7.7 Hz). ^{1}H NMR (DMSO-d_6): δ 2.32s (6H, N–CH_3), 3.40s [3H, (S_2C)N–CH_3 (A)], 3.42s [3H, (S_2C)N–CH_3 (B)], 3.67s (2H, –CH_2–), 7.17m (3H, $H_{3\text{-}5}$), 7.54d (1H, H_6, $^3J_{HH}$ 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 42.88 [(S_2C)N–CH$_3$ (A)], 43.86 (N–CH$_3$), 46.67 [(S_2C)N–CH$_3$ (B)], 64.01 (–CH$_2$–), 125.89, 127.03 ($C_{3,4}$), 128.13 (C_5), 129.66 (C_6), 136.22 (C_2), 138.45 (C_1), 198.24 [(S_2C)N–CH$_3$]. ^{13}C NMR (DMSO-d_6): δ 42.63 [(S_2C)N–CH$_3$ (A)], 43.50 (N–CH$_3$), 46.08 [(S_2C)N–CH$_3$ (B)], 63.04 (–CH$_2$–), 125.94, 127.28 ($C_{3,4}$), 127.91 (C_5), 129.01 (C_6), 135.61 (C_2), 138.42 (C_1), 195.81 [(S_2C)N–CH$_3$]. ^{77}Se NMR ($CDCl_3$): δ 631.9.

4.7. Preparation of [2-(dimethylaminomethyl)phenyl] selenium(II) diethyldithiocarbamate, [2-(Me_2NCH_2)-C_6H_4]SeS(S)$CNEt_2$ (**7**)

A mixture of **3** (0.40 g, 1.36 mmol) and Na[S_2CNE-t_2] · 3H_2O (0.31 g, 1.38 mmol) in 25 ml anhydrous CH_2Cl_2 was stirred at room temperature for 12 h. The reaction mixture was filtered to remove NaBr and the clear yellowish filtrate was concentrated in vacuo until a yellowish solid deposited. The product was separated

Table 3
X-ray crystal data and structure refinement for compounds **2**, **4**–**8**

	2	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_9H_{12}ClNSe$	$C_9H_{12}INSe$	$C_9H_{12}Cl_3NSe$	$C_{12}H_{18}N_2S_2Se$	$C_{14}H_{22}N_2S_2Se$	$C_{23}H_{28}N_2P_2S_2Se$
Formula weight	248.61	340.06	319.51	333.36	361.42	537.49
T (K)	100(2)	100(2)	297(2)	297(2)	120(2)	297(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	*Pbca*
Unit cell dimensions						
a (Å)	7.6313(6)	8.1066(4)	7.212(18)	8.440(12)	7.873(5)	9.166(12)
b (Å)	10.8436(8)	10.900(1)	7.236(2)	8.927(1)	8.484(1)	18.450(2)
c (Å)	23.539(2)	23.585(1)	12.533(3)	19.368(3)	24.935(2)	30.212(4)
α (°)			80.732(4)			
β (°)			76.633(4)	90.047(2)		
γ (°)			74.151(4)			
Volume (Å^3)	1947.8(3)	2084.0(2)	608.8(3)	1459.3(4)	1665.4(2)	5109.2(12)
Z	8	8	2	4	4	8
D_{calc} (g cm^{-3})	1.696	2.168	1.743	1.517	1.441	1.398
Absorption coefficient (mm^{-1})	4.074	6.515	3.704	2.840	2.495	1.772
$F(000)$	992	1280	316	680	744	2208
Crystal size (mm)	$0.50 \times 0.50 \times 0.45$	$0.40 \times 0.40 \times 0.30$	$0.32 \times 0.20 \times 0.13$	$0.42 \times 0.28 \times 0.25$	$0.02 \times 0.02 \times 0.01$	$0.32 \times 0.28 \times 0.12$
θ range for data collection (°)	3.18 to 27.54	3.05 to 27.49	1.68 to 26.37	2.10 to 26.37	3.06 to 27.47	2.21 to 26.34
Reflections collected	17037	18795	4896	11312	4500	38719
Independent reflections	2236 [R_{int} = 0.0358]	2398 [R_{int} = 0.0288]	2443 [R_{int} = 0.0186]	2981 [R_{int} = 0.0253]	2579 [R_{int} = 0.0440]	5213 [R_{int} = 0.0668]
Data/restraints/parameters	2236/0/111	2398/0/111	2443/0/129	2981/0/158	2579/0/176	5213/0/275
Goodness-of-fit on F^2	1.057	1.077	1.055	1.061	1.045	1.113
Final R indices[a]						
R_1	0.0279	0.0298	0.0283	0.0288	0.0368	0.0507
wR_2	0.0665	0.0714	0.0719	0.0714	0.0852	0.1000
R indices (all data)						
R_1	0.0402	0.0331	0.0318	0.0363	0.0469	0.0702
wR_2	0.0719	0.0732	0.0736	0.0747	0.0889	0.1067
Extinction coefficient					−0.002(12)	
Largest difference peak and hole (e Å^{-3})	0.733 and −0.390	2.919 and −0.406	0.676 and −0.446	0.355 and −0.19	0.681 and −0.559	0.439 and −0.404

[a] $F^2 > 4\sigma(F^2)$ for **2**, **4** and **7**, and $[I > 2\sigma(I)]$ for **5**, **6** and **8**, respectively.

by filtration and recrystallized from CH_2Cl_2/*n*-hexane (1:5, v/v) to give **7** as a pale yellow solid. Yield: 0.3 g (61%). M.p. 68–70 °C. Anal. Found: C, 46.37; H, 5.91; N, 7.58. Calc. for $C_{14}H_{22}N_2S_2Se$: C, 46.53; H, 6.14; N, 7.75%. ^{1}H NMR: δ 1.30t [3H, N–CH_2CH_3 (A), $^3J_{HH}$ 6.7 Hz], 1.36t [3H, N–CH_2CH_3 (B), $^3J_{HH}$ 6.7 Hz], 2.38s (6H, N–CH_3), 3.66s (2H, –CH_2–), 3.95q [2H, N–CH_2CH_3 (B), $^3J_{HH}$ 6.8 Hz], 4.11q (2H, N–CH_2CH_3 (A), $^3J_{HH}$ 6.8 Hz), 7.08m (2H, $H_{3,4}$), 7.18ddd (1H, H_5, $^3J_{HH}$ 8.0, $^3J_{HH}$ 8.0, $^4J_{HH}$ 2.0 Hz), 7.70d (1H, H_6, $^3J_{HH}$ 7.9 Hz). ^{13}C NMR: δ 11.60 [N–CH_2CH_3 (A)], 13.02 [N–CH_2CH_3 (B)], 43.81 (N–CH_3), 47.77 [N–CH_2CH_3 (B)], 50.72 [N–CH_2CH_3 (A)], 64.01 (–CH_2–), 125.79, 126.98 ($C_{3,4}$), 128.04 (C_5), 129.68 (C_6), 136.32 (C_2), 138.48 (C_1), 196.48 [(S_2C)N–CH_2CH_3].

4.8. Preparation of [2-(dimethylaminomethyl)-phenyl]selenium(II) P, P-dimethyl-P′,P′-diphenyl-dithiodiphosphinate, [2-(Me_2NCH_2)C_6H_4]Se–S–PMe_2=N–PPh_2=S (**8**)

A mixture of **3** (0.27 g, 0.92 mmol) and K[($SPMe_2$)($SPPh_2$)N] (0.33 g, 0.91 mmol) in 25 ml anhydrous CH_2Cl_2 was stirred at room temperature for 12 h. Then the KBr was filtered off and the clear yellow solution was concentrated in vacuo until a yellow solid deposited. The solid was separated by filtration and recrystallized from CH_2Cl_2/*n*-hexane (1:5, v/v) to give yellow crystals of **8**. Yield: 0.27 g (55%). M.p. 108–110 °C. Anal. Found: C, 51.03; H, 4.98; N, 5.11. Calc. for $C_{23}H_{28}N_2P_2S_2Se$: C, 51.39; H, 5.25; N, 5.21%. ^{1}H NMR: δ 1.99 d (6H, P–CH_3, $^2J_{PH}$ 13.1 Hz), 2.33s (6H, N–CH_3), 3.67s (2H, –CH_2–), 7.08dd (1H, H_3, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.1 Hz), 7.13ddd (1H, H_4, $^3J_{HH}$ 7.3, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.1 Hz), 7.22ddd (1H, H_5, $^3J_{HH}$ 7.6, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.6 Hz), 7.29m (6H, P–C_6H_5-*meta* + *para*), 7.95dm (4H, P–C_6H_5-*ortho*, $^3J_{PH}$ 13.6 Hz), 8.02dd (1H, H_6, $^3J_{HH}$ 8.0, $^4J_{HH}$ 0.8 Hz). ^{13}C NMR: δ 21.42dd (P–CH_3, $^1J_{PC}$ 71.1, $^3J_{PC}$ 3.2 Hz), 43.94 (N–CH_3), 63.73 (–CH_2–), 126.16 (C_4), 126.91 (C_3), 127.60d (C_6H_5-*meta*, $^3J_{PC}$ 12.9 Hz), 128.37 (C_5), 129.58d (C_6H_5-*para*, $^4J_{PC}$ 2.7 Hz), 129.88 (C_6), 130.67d (C_6H_5-*ortho*, $^2J_{PC}$ 11.2 Hz), 135.18 (C_1), 137.97 (C_2), 141.34dd (C_6H_5-*ipso*, $^1J_{PC}$ 107.4, $^3J_{PC}$ 6.1 Hz). ^{31}P NMR: δ 40.8d (Me_2P-S, $^3J_{PP}$ 8.3, $^1J_{PC}$ 71.1 Hz), 42.6d (Ph_2P=S, $^3J_{PP}$ 8.3, $^1J_{PC}$ 107.7 Hz). ^{77}Se NMR ($CDCl_3$): δ 579.9.

4.9. X-ray structure determination

Block crystals of [(2-Me_2NCH_2)C_6H_4]SeCl (**2**) (very pale yellow), [(2-Me_2NCH_2)C_6H_4]SeI (**4**) (red), [(2-Me_2NCH_2)C_6H_4]$SeCl_3$ (**5**) (yellow), [2-(Me_2NCH_2)-C_6H_4]SeS(S)CNMe_2 (**6**) (yellow), [2-(Me_2NCH_2)C_6H_4]-SeS(S)CNEt_2 (**7**) (colourless) and [2-(Me_2NCH_2)C_6H_4] Se–S–PMe_2=N–PPh_2=S (**8**) (yellow) were mounted on glass fibres (**2**, **4**, and **7**) and cryoloops (**5**, **6**, and **8**), respectively. For **2**, **4**–**6**, and **8**, a hemisphere of data were collected on a Bruker APEX CCD diffractometer using a counting time of 20 s (**2**, **4**) or 10 s (**5**, **6**, and **8**) per frame. For **7** the data were collected on an Enraf Nonius KappaCCD area detector diffractometer, with φ and ω scans chosen to give a complete asymmetric unit. Data reduction was performed using the SAINT [48] (for **2**, **4**–**6**, and **8**) and DENZO [49] (for **7**) software and the data were corrected for Lorentz, polarization and absorption effects using the SAINT and SADABS programs. Cell refinement gave cell constants corresponding to orthorhombic (for **2**, **4**, **7**, and **8**), triclinic (for **5**) and monoclinic (for **6**) cells whose dimensions are given in Table 3 along with other experimental parameters.

The structures were solved by direct methods [50] and refined using the WINGX (**2**, **4**, and **7**) [51] and SHELXTL (**5**, **6**, and **8**) [52] versions of SHELX-97 [53]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement converged (largest parameter shift was 0.001 times its e.s.d.). The drawings were created with the DIAMOND program [54].

5. Supplementary material

Crystallographic data for the structural analysis of compounds **2**, **4**–**8** have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 250623 (**2**), 250622 (**4**), 250773 (**5**), 250772 (**6**), 250621 (**7**) and 250771 (**8**). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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