Group 12 metal aryl selenolates. Crystal and molecular structure of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ and [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$M (M = Zn, Cd)

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ABSTRACT

Diorganodiselenide [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**1**) was obtained by hydrolysis/oxidation of the corresponding [2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeLi derivative. The treatment of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ with elemental sodium in THF resulted in [2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeNa (**2**). Reactions between alkali metal selenolates [2-(R$_2$NCH$_2$)C$_6$H$_4$]SeM′ (R = Me, Et; M′ = Li, Na) and MCl$_2$ (M = Zn, Cd) in a 2:1 molar ratio resulted in the [2-(R$_2$NCH$_2$)C$_6$H$_4$Se]$_2$M species [R = Me, M = Zn (**3**), Cd (**4**); R = Et, M = Zn (**5**), Cd (**6**)]. The new compounds were characterized by multinuclear NMR (^{1}H, ^{13}C, ^{77}Se, ^{113}Cd) and mass spectrometry. The crystal and molecular structures of **1**, **3** and **4** revealed monomeric species stabilized by N → Se (for **1**) and N → M (for **3** and **4**) intramolecular interactions.

1. Introduction

Organoselenium and -tellurium compounds containing an intramolecular N → E (E = Se, Te) interaction have attracted much interest in the last two decades, mainly due to their increased stability as monomeric species and their applications in biology, asymmetric synthesis, catalysis or microelectronics [1–18]. The presence of an organic group containing donor atoms capable for intramolecular coordination favoured also the isolation of monomeric metal chalcogenolates [19–25]. Of special interest are Group 12 metal complexes which are considered to be good candidates as single-source precursors for CVD processes [21–25]. In order to obtain M/E thin films of good quality by such processes, compounds with monomeric structure, thermal stability and high volatility are required. Even medium sized organic groups were observed to result in dimeric or polymeric [M(ER)$_2$]$_n$ species (M = Zn, Cd, Hg; E = S, Se, Te; R = Ph, n-Bu, 4-CH$_3$C$_6$H$_4$, 2,4,6-Me$_3$C$_6$H$_2$) [22,25–32]. However, it was noted that such complexes decompose thermally with formation of ME and ER$_2$ species [21,22,33]. Different

strategies were used in order to stablize monomeric species and to avoid polymerization, i.e. (i) the use of organochalcogenolato ligands with bulky substituents, (ii) the increase of the coordination number to the metal centre by additional neutral ligands [22,28], or (iii) combination of the advantages of both the above approaches by using organic groups containing donor atoms capable for intramolecular coordination [21–25]. While bulky substituents in many cases generate compounds which eliminate diorganodichalcogenides, thus resulting in elemental metal, and dissociation of neutral ligands before the sublimation temperature was observed, the last method seems to be a more attractive way to increase the thermal stability and to prevent polymerization.

We have reported recently on the synthesis, solution behaviour and molecular structures of various hypervalent organoselenium compounds containing organic groups with pendant arms, i.e. 2-(Me$_2$NCH$_2$)C$_6$H$_4$ [34] or 2-{X(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$ (X = O, NMe) [35,36]. As a continuation of our previous studies on organoselenium compounds we report here on the synthesis and structural characterization, both in solution and solid state, of the new hypervalent diorganodiselenide [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ as well as the new Group 12 metal complexes, [2-(R$_2$NCH$_2$)C$_6$H$_4$Se]$_2$M (R = Me, Et; M = Zn, Cd).

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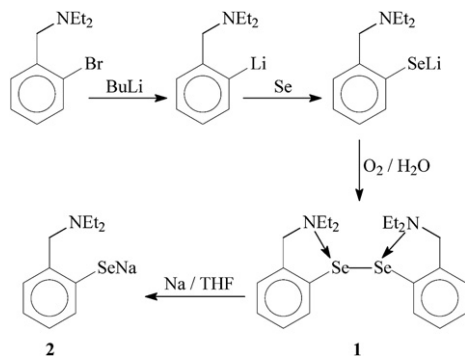
Scheme 1.

2. Results and discussion

2.1. Preparation and spectroscopic characterization

The new diorganodichalcogenide [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**1**) was obtained using the *ortho*-lithiation route. The organolithium reagent [2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li was prepared as a white solid by direct lithiation of the corresponding 2-(*N*,*N*-diethylaminomethyl)benzene bromide with *n*-BuLi, in anhydrous hexane. The treatment of a THF solution of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]Li with finely grounded selenium powder, under argon, followed by hydrolysis and air oxidation, resulted in isolation of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (Scheme 1).

Reaction of the appropriate alkali metal aryl selenolate [{2-(R$_2$NCH$_2$)C$_6$H$_4$}Se]M′ (M′ = Li, Na) with ZnCl$_2$ or CdCl$_2$, respectively, in a 2:1 molar ratio, afforded isolation of [{2-(R$_2$NCH$_2$)C$_6$H$_4$}Se]$_2$M (R = Me, Et, M = Zn, Cd) (Scheme 2). The lithium 2-(*N*,*N*-dimethylaminomethyl)selenolate was obtained as previously described [37]. The sodium 2-(*N*,*N*-diethylaminomethyl)selenolate (**2**) was prepared by reacting [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ with sodium, in anhydrous THF, and was isolated as a colorless, solid powder, extremely sensitive to moisture.

The compounds were isolated as yellow (**1** and **6**), pale yellow (**3**) or colorless (**4** and **5**) solids and were recrystallized from a CH$_2$Cl$_2$/*n*-hexane mixture. Elemental analyses and NMR data are consistent with the anticipated formulations.

At low pressure (10^{-3} atm) the methyl substituted complex **3** sublime without decomposition at 162 °C.

2.2. Spectroscopy

The NMR (^{1}H, ^{13}C) spectra, recorded in CDCl$_3$ solution, at room temperature, for compound **1** provided no evidence for the presence of N → Se intramolecular interactions in solution. The resonance for the methylene protons of the pendant C*H*$_2$NEt$_2$ arm appears as singlet at δ 3.72 ppm. The ethyl organic groups attached to nitrogen show the expected resonances, *i.e.* a quartet at δ 2.61 and a triplet at δ 1.06 ppm.

In the case of the sodium aryl selenolate **2** the ^{1}H NMR spectrum in THF-d_8 solution revealed a similar behavior for the pendant
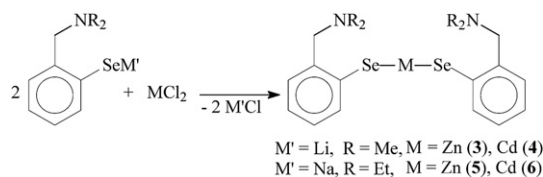
Scheme 2.

C*H*$_2$NEt$_2$ group, with singlet resonance for the C*H*$_2$NEt$_2$ protons and equivalent ethyl groups attached to nitrogen.

The ^{1}H NMR spectrum of complex **3** in CDCl$_3$ solution suggests the coordination of the nitrogen atom even at room temperature. The C*H*$_2$ protons and the methyl groups gave an AB spin system with δ$_A$ 3.14 and δ$_B$ 4.06 ppm and two singlet resonances at δ 1.65 and 2.54 ppm, respectively. In case of the cadmium(II) complexes **4** and **6** and the zinc(II) complex **5** broad resonances were observed at 25 °C, thus suggesting a fast dynamic process in solution.

For complex [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}Se]$_2$Cd (**4**) the ^{113}Cd NMR spectrum exhibits one resonance at δ −196.2 ppm, consistent with the presence of only one species in solution. For this compound a variable temperature ^{1}H NMR experiment was performed in CDCl$_3$ solution. At 213 K a spectrum corresponding to the frozen structure was obtained, showing an AB spin system for the methylene protons (δ$_A$ 2.88 and δ$_B$ 4.22 ppm) and two singlet resonances (δ 1.25 and 2.56 ppm) for the methyl protons. For both types of protons coalescence was achieved at 268 K and a free enthalpy ΔG$^{\#}$ of 54.5 kJ mol^{-1} was calculated for the corresponding dynamic processes.

For compound **3** the temperature of coalescence was 328 K in C$_6$D$_6$ and the calculated medium free enthalpy was ΔG$^{\#}$ 66.2 kJ mol^{-1} (66.1 for the C*H*$_2$ protons and 66.3 kJ mol^{-1} for the C*H*$_3$ groups, respectively). For the ethyl substituted derivatives **5** and **6** free enthalpies of 56.7 and 55.1 kJ mol^{-1} were calculated at 268 K, respectively, for the dynamic process in which the C*H*$_2$N protons are involved. At low temperature the aliphatic region corresponding to the ethyl groups becomes very complex, due to their non-equivalence and the proton–proton couplings.

The ^{77}Se NMR spectra are consistent with the formation of the metal complexes, the corresponding resonances (δ −81.2 for **3**, −111.5 for **4**, −59.0 for **5** and −95.0 ppm for **6**) being strongly upfield shifted with respect to the resonances observed for [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (δ 430 ppm [37]) or **1** (δ 427.4 ppm).

The EI mass spectra for compounds **3** and **4** show peaks corresponding to the molecular ion [*m*/*z* 492 for **3** (97%) and 542 for **4** (29%)] as well as fragments of lower mass, *e.g.* [2-(Me$_2$NCH$_2$)C$_6$H$_4$SeM$^+$] [*m*/*z* 278 for **3** (23%) and 326 for **4** (8%)], [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se+H$^+$] [*m*/*z* 214 (68% for **3** and 100% for **4**)] and [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$^+$ [*m*/*z* 134 (100% for **3** and 34% for **4**)]. The ESI mass spectra for all four complexes, in addition to the molecular ion and [2-(R$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$]$^+$ species, exhibit also ions with mass exceeding that of the corresponding monomer, *i.e.* *m*/*z* 770 [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_3$Se$_3$Zn$_2^+$], *m*/*z* 866 [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_3$Se$_3$Cd$_2^+$], *m*/*z* 853 [{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_3$Se$_3$Zn$_2^+$] and *m*/*z* 948 [{2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_3$Se$_3$Cd$_2^+$], thus suggesting that in vapor phase dinuclear species are also present. This behavior suggests that thermal decomposition occurs by releasing the corresponding diorganodiselenide.

2.3. Crystal and molecular structure of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**1**)

Single crystals of the diselenide **1** suitable for X-ray diffraction studies were obtained from a CH$_2$Cl$_2$/*n*-hexane mixture (1/5, v/v). The crystal contains discrete molecules. Selected interatomic distances and angles are listed in Table 1, while the ORTEP-like diagram is depicted in Fig. 1.

Intramolecular selenium–nitrogen interactions of significant strength are established in the diorganodiselenide **1**, *i.e.* N1⋯Se1 2.713(5) and N2⋯Se2 3.068(6) Å (*cf.* Σr_{vdW} (Se,N) 3.54 Å [38]), of similar magnitude with those observed in other related derivatives, *e.g.* [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ [2.856(3)/2.863(4) Å] [37], [2-{O(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]$_2$Se$_2$ [2.813(2)/2.825(3) Å], [2-{MeN(CH$_2$CH$_2$)$_2$NCH$_2$}C$_6$H$_4$]$_2$Se$_2$ [3.135(3)/2.7393(3) Å] [36], bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide [2.819(5)/2.705(5) Å] [39]. Due to the intramolecular N → Se interactions a distorted T-shaped geometry is achieved around each selenium atom.

Table 1
Selected interatomic distances (Å) and angles (°) in compounds [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**1**), [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Zn (**3**) and [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Cd (**4**).

1		3		4a		4b	
N1–Se1	2.713(5)	Zn1–Se1	2.390(2)	Cd1–Se1	2.534(1)	Cd2–Se3	2.519(1)
N2–Se2	3.068(6)			Cd1–Se2	2.546(1)	Cd2–Se4	2.517(1)
Se1–Se2	2.3544(11)	Zn1–N1	2.124(5)	Cd1–N1	2.397(8)	Cd2–N3	2.400(8)
				Cd1–N2	2.360(7)	Cd2–N4	2.362(9)
N2–Se2–Se1	174.6(1)	Se1–Zn1–Se1′	131.45(8)	Se1–Cd1–Se2	142.01(5)	Se3–Cd2–Se4	141.5(5)
Se2–Se1–N1	169.5(1)	N1–Zn1–N1′	119.8(3)	N1–Cd1–N2	110.7(3)	N3–Cd2–N4	108.1(5)
N2–Se2–C12	71.5(2)	N1–Zn1–Se1	101.0(2)	N1–Cd1–Se1	94.5(2)	N3–Cd2–Se3	94.2(2)
C12–Se2–Se1	103.3(2)	N1′–Zn1–Se1	102.8(2)	N2–Cd1–Se1	106.97(2)	N4–Cd2–Se3	108.1(2)
C1–Se1–N1	74.9(2)	C1–Se1–Zn1	98.8(2)	N1–Cd1–Se2	107.97(2)	N3–Cd2–Se4	107.2(2)
C1–Se1–Se2	100.8(2)	C9–N1–C8	108.8(5)	N2–Cd1–Se2	93.5(2)	N4–Cd2–Se4	95.4(2)
C10–N1–C7	110.7(5)	C9–N1–C7	109.6(5)	C1–Se1–Cd1	89.9(3)	C19–Se3–Cd2	91.2(3)
C10–N1–C8	114.9(6)	C8–N1–C7	107.4(5)	C10–Se2–Cd1	88.5(3)	C28–Se4–Cd2	88.0(4)
C7–N1–C8	112.2(5)	C9–N1–Zn1	109.8(4)	C9–N1–C8	109.3(9)	C27–N3–C25	108.1(8)
C7–N1–Se1	89.9(3)	C8–N1–Zn1	110.3(4)	C9–N1–C7	111.6(8)	C27–N3–C26	106.7(8)
C8–N1–Se1	108.6(3)	C7–N1–Zn1	110.9(3)	C8–N1–C7	108.7(8)	C25–N3–C26	110.1(8)
C10–N1–Se1	117.9(4)			C9–N1–Cd1	114.9(6)	C27–N3–Cd2	106.6(7)
C18–N2–C21	112.5(7)			C8–N1–Cd1	104.6(7)	C25–N3–Cd2	107.9(5)
C18–N2–C19	111.3(7)			C7–N1–Cd1	107.5(6)	C26–N3–Cd2	117.1(6)
C21–N2–C19	110.5(7)			C17–N2–C18	108.5(7)	C34–N4–C35	109.9(9)
C18–N2–Se2	78.4(4)			C17–N2–C16	108.5(8)	C34–N4–C36	109.3(9)
C19–N2–Se2	124.3(5)			C18–N2–C16	108.8(7)	C35–N4–C36	108.5(10)
C21–N2–Se2	115.5(5)			C17–N2–Cd1	106.2(6)	C34–N4–Cd2	107.6(8)
				C18–N2–Cd1	115.7(5)	C35–N4–Cd2	115.0(6)
				C16–N2–Cd1	108.9(5)	C36–N4–Cd2	106.4(7)

The intramolecular N → Se coordination results in five-membered SeC$_3$N rings, folded along the imaginary Se···C$_{methylene}$ axis, with nitrogens displaced out of the best SeC$_3$ planes. This induces planar chirality, with nitrogen as pilot atom and the aromatic ring as chiral plane, similarly to the situation described for other related diselenides [36–38]. As a consequence the compound crystallizes as a racemate, *i.e.* 1:1 mixtures of (R_{N1},S_{N2}) and (S_{N1},R_{N2}) isomers, with respect to the two chelate rings in a molecular unit.

2.4. Crystal and molecular structure of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$M [M = Zn (**3**), Cd (**4**)]

Single crystals of the complexes **3** and **4** suitable for X-ray diffraction studies were obtained from a CH$_2$Cl$_2$/n-hexane mixture (1/5, v/v). Relevant interatomic distances and angles are listed in Table 1, while the ORTEP-like diagrams are depicted in Figs. 2 and 3, respectively. For the cadmium derivative two independent molecules are present in the unit cell.

In both compounds the organoselenolato groups behave as monometallic biconnective moieties, being attached to the metal centre covalently by selenium [Zn1–Se1 2.390(2) Å in **3**; Cd1–Se1
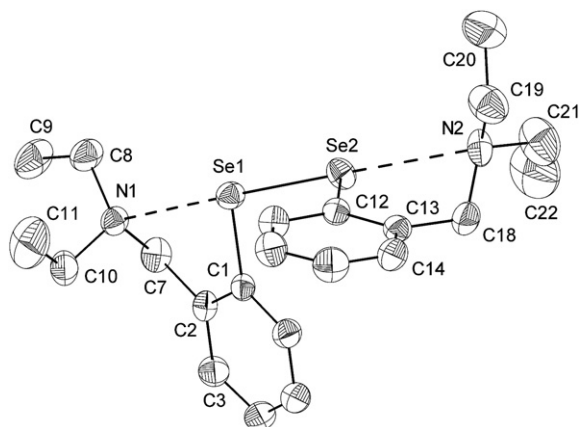
2.534(1)/Cd1–Se2 2.546(1) Å in **4a** and Cd2–Se3 2.519(1)/Cd2–Se4 2.517(1) Å in **4b**] and secondary by the nitrogen of the pendant arms.

The crystal of complex **3** consists of centrosymmetric discrete molecules separated by normal van der Waals distances. Due to the strong intramolecular N → Zn coordination [Zn1–N1 2.124(5) Å; *cf.* Σr_{vdW}(N,Zn) 2.94 Å] [38], a distorted tetrahedral geometry is achieved around the metal centre, with a dihedral angle of 73.1° between Zn1Se1N1 and Zn1Se1′N1′ planes. The two ZnSeC$_3$N metallacycles have boat conformations with selenium and C$_{methylene}$ atoms in apices. The intramolecular N → Zn coordination induces planar chirality. Compound **3** crystallizes in the chiral space group $P2(1)2(1)2(1)$ (orthorhombic) and therefore the investigated crystal contains only the (R_{N1},$R_{N1'}$) isomer.

The molecules of the cadmium complex **4** are similar to those of the Zn analogue **3** with respect to the tetrahedral environment of the metal centre. In both independent molecules the two six-membered metallacycles formed per metal atom due to strong intramolecular N → Cd coordination [Cd1–N1 2.397(8)/Cd1–N2 2.360(7) Å in **4a**, and Cd2–N3 2.400(8)/Cd2–N4 2.362(9) Å in **4b**; *cf.* Σr_{vdW}(N,Cd) 3.14 Å] [38] exhibit again twisted boat conformations with selenium and the C$_{methylene}$ atoms in apices. For the resulted CdSe$_2$N$_2$ cores the dihedral angles between the planes Cd1N1Se1/Cd1N2Se2 and Cd2N3Se3/Cd2N4Se4 are 79.1° for **4a** and 81.3° for **4b**, respectively.

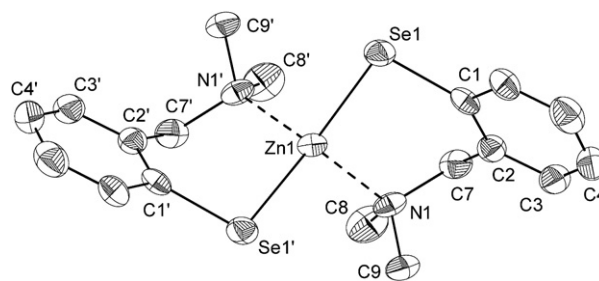**Fig. 1.** ORTEP-like representation at 30% probability and atom numbering scheme for isomer [R_{N1},S_{N2}] − **1** (hydrogen atoms are omitted for clarity).

Fig. 2. ORTEP-like representation at 30% probability and atom numbering scheme for isomer R_N-**3** [symmetry equivalent position (1 − x, 1 − y, z) is given by "prime"; hydrogen atoms are omitted for clarity].
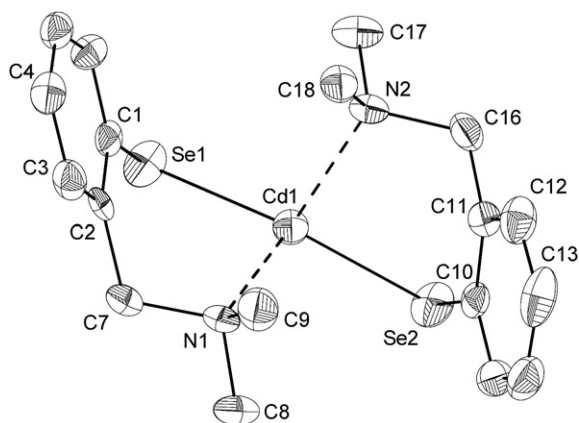
Fig. 3. ORTEP-like representation at 30% probability and atom numbering scheme for isomer S_{N1},S_{N2}–**4a** (hydrogen atoms are omitted for clarity).

Due to the planar chirality induced by the intramolecular N → Cd coordination the compound crystallizes as a 1:1 mixture of $(R_{N1},R_{N2})/(S_{N1},S_{N2})$–**4a** and $(R_{N3},R_{N4})/(S_{N3},S_{N4})$–**4b** isomers.

The main difference in the molecular structure of the two derivatives consists in the orientation of the aromatic rings in the molecular unit with respect to the best plane described by the nitrogen and the methylene carbon atoms. In the zinc(II) complex **3** the two C_6H_4 rings are placed on the same side of the N_2C_2 plane as are the selenium and the metal atoms, so that any intramolecular $C-H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contact is prevented (Scheme 3a). By contrast, in the cadmium(II) complex **4** the aromatic rings are placed on opposite side of the N_2C_2 plane with respect to the selenium and the metal atoms (Scheme 3b). This brings the aromatic rings closer to the methyl groups attached to nitrogen and weak $C-H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contacts are established [C9–H9B⋯$Ph_{centroid}$(C10–C15) 2.85 Å and C18–H18C⋯$Ph_{centroid}$(C1–C6) 3.03 Å for **4a**; C26–H26A⋯$Ph_{centroid}$(C28–C33) 2.87 Å and C35–H35B⋯$Ph_{centroid}$(C19–C24) 3.01 Å for **4b**].

Additional intermolecular $C-H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contacts result in a layer arrangement in the crystal of **3**, each molecule being connected to other four neighboring molecules [C9–H9A⋯$Ph_{centroid}$ 3.04 Å]. Chain polymers of alternating (S_{N1},S_{N2})–**4a**/(R_{N3},R_{N4})–**4b** and (R_{N1},R_{N2})–**4a**/(S_{N3},S_{N4})–**4b** molecules, respectively, can be considered in the crystal of the cadmium complex, for each molecule only one aromatic ring being involved [C18–H18B⋯$Ph_{centroid}$ 2.97 Å and C26–H26B⋯$Ph_{centroid}$ 3.06 Å]. No further interactions are present between the parallel chains (see also Supplementary material).

3. Conclusions

The new diorganodichalcogenide $[2-(Et_2NCH_2)C_6H_4]_2Se_2$, as well as group 12 metal selenolates of type $[2-(R_2NCH_2)C_6H_4Se]_2M$

($R = Me$, Et; $M = Zn$, Cd) were prepared and structurally characterized. $[2-(Et_2NCH_2)C_6H_4]_2Se_2$ diorganodiselenide exhibits a similar structure in solution and in solid state as found for related diorganodiselenides with nitrogen-containing pendant arm aryl groups. The group 12 metal selenolates have monomeric structures in solid-state, stabilized by intramolecular N → M interactions. The mass spectra suggest the release of diorganodiselenide by thermal decomposition in case of all four metal complexes.

4. Experimental

4.1. Materials and procedures

Starting materials were commercially available: selenium powder, butyllithium (1.6 M in hexane), 2-bromobenzyl bromide, $ZnCl_2$, $CdCl_2$ (Fluka) or prepared according to literature methods ($[2-(Me_2NCH_2)C_6H_4]SeLi$ [37]). $ZnCl_2$ and $CdCl_2$ were dehydrated before using. All manipulations were carried out under argon using Schlenk techniques. Solvents were dried and distilled prior to use. Elemental analyses were performed on a VarioEL analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. Multinuclear NMR spectra were recorded in dry $CDCl_3$, C_6D_6, CD_2Cl_2 or THF-d_8 on a BRUKER AVANCE 300 instrument operating at 300.1, 75.5 and 57.26 MHz for ^1H, ^{13}C and ^{77}Se, respectively, or a Bruker 500 machine operating at 500 and 111 MHz for ^1H and ^{113}Cd, 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; THF-d_8: ^1H 1.73 and 3.58, ^{13}C 25.4 and 67.6 ppm, CD_2Cl_2: ^1H 5.24 ppm, C_6D_6: ^1H 7.15 ppm). ^1H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HMQC and HMBC). The ^{77}Se spectra were obtained using diphenyl diselenide as external standard. Chemical shifts are reported relative to dimethyl selenide (δ 0 ppm) by assuming that the resonance of the standard is at δ 461 ppm [40]. Mass spectra were recorded on a FINNIGAN MAT 8200 spectrometer (EI) or an Agilent 6320 Ion Trap instrument (ESI).

4.2. Synthesis of $[2-(Et_2NCH_2)C_6H_4]_2Se_2$ (**1**)

A solution of ^nBuLi in hexane (1.6 M, 27 mL) was added dropwise to a stirred solution of 2-(N,N-diethylaminomethyl)benzene bromide (10.483 g, 43.29 mmol) in 150 mL anhydrous hexane, at room temperature. The reaction mixture was stirred at room temperature for 24 h, when a white slurry of the lithiated product was obtained. The white precipitate was separated by filtration and washed with 3×30 mL hexane, yielding 2.38 g (30.6%) of the lithiated derivative. The solid product (2.38 g, 14.06 mmol) was disolved in 100 mL THF and selenium powder (1.11 g, 14.05 mmol) was added. The reaction mixture was stirred for 2 h at room temperature. The resulting yellowish solution was poured into a beaker containing water (100 mL) and left overnight in an
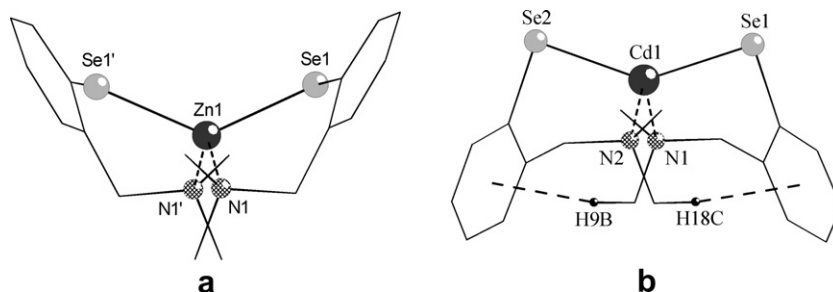
Scheme 3.

Table 2
X-ray crystal data and structure refinement for compounds [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (**1**), [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Zn (**3**) and [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Cd (**4**).

	1	3	4
Empirical formula	C$_{22}$H$_{32}$N$_2$Se$_2$	C$_{18}$H$_{24}$N$_2$Se$_2$Zn	C$_{18}$H$_{24}$CdN$_2$Se$_2$
Formula weight	482.42	491.68	538.71
Temperature (K)	297(2)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P2(1)/c	P2(1)2(1)2(1)	P2(1)/c
Unit cell dimensions			
a (Å)	8.626(3)	10.262(13)	10.980(2)
b (Å)	9.632(3)	14.613(19)	9.402(2)
c (Å)	27.802(9)	6.559(8)	38.481(8)
α (°)	90	90	90
β (°)	98.457(7)	90	90.890(4)
γ (°)	90	90	90
Volume (Å^3)	2284.7(12)	984(2)	3972.1(15)
Z	4	2	8
D_c (g/cm^3)	1.402	1.660	1.802
Absorption coefficient (mm^{-1})	3.245	4.950	4.765
F(000)	984	488	2096
Crystal size, mm	0.31 × 0.30 × 0.27	0.40 × 0.37 × 0.30	0.48 × 0.37 × 0.28
θ range for data collections (°)	2.24–25.00	2.43–25.00	2.12–25.00
Reflections collected	10,683	4960	27,874
Independent reflections	3999 [R(int) = 0.0553]	1740 [R(int) = 0.0451]	6985 [R(int) = 0.0726]
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	3999/0/239	1740/0/107	6985/0/423
Goodness-of-fit on F^2	1.143	1.050	1.187
Final R indices [$F^2 > 2\sigma(F^2)$]	R1 = 0.0719, wR2 = 0.1289	R1 = 0.0436, wR2 = 0.0835	R1 = 0.0777, wR2 = 0.1375
R indices (all data)	R1 = 0.1024, wR2 = 0.1394	R1 = 0.0537, wR2 = 0.0872	R1 = 0.1068, wR2 = 0.1477
Largest diff. peak and hole, eÅ^{-3}	0.537 and −0.537	0.373 and -0.494	1.002 and -1.239

efficient fume hood for a complete oxidation. The organic phase was separated and the aqueous phase was extracted several times with methylene chloride. The combined organic phases were dried over anhydrous MgSO$_4$. Evaporation of the solvent gave 2 g (59%) of the title compound as a pale yellow solid. M.p. 55 °C. Anal. Found: C 54.83; H 6.82, N 6.11%. Calc. for C$_{22}$H$_{32}$N$_2$Se$_2$ (M = 482.43): C 54.77, H 6.69, N 5.81%. ^{1}H (CDCl$_3$, 300 MHz): δ 1.06 t (12H, NCH$_2$CH_3, $^3J_{HH}$ 7.1 Hz), 2.61q (8H, NCH_2CH$_3$, $^3J_{HH}$ 7.1 Hz), 3.72s (4H, CH_2N), 7.13 m (6H, C$_6$H$_4$, H_{3-5}), 7.80dd (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 6.8, $^4J_{HH}$ 2.1 Hz). ^{13}C (CDCl$_3$, 75.5 MHz): δ 10.87 (NCH$_2$CH_3), 45.2 (NCH_2CH$_3$), 59.05 (CH_2N), 125.57 (C$_5$), 127.83 (C$_4$), 128.35 (C$_3$), 131.17 (C$_6$), 133.74 (C$_2$), 139.84 (C$_1$). ^{77}Se (CDCl$_3$, 57.26 MHz): δ 427.4.

4.3. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeNa (2)

[2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (4 g, 8.29 mmol) was dissolved in 100 mL anhydrous THF under argon atmosphere. The THF solution was added to a sodium mirror previously obtained in a round bottom flask and left to react under stirring, at room temperature, overnight. The resulting red clear solution was filtered off from sodium and the solvent was evaporated at reduced pressure. The obtained white solid was washed twice with hexane (2 × 10 mL) to remove all unreacted diselenide and dried in vacuum. Yield 3.59 g (82%). ^{1}H NMR (300 MHz, THF-d_8): δ 1.03 t (6H, NCH$_2$CH_3, $^3J_{HH}$ 7.1 Hz), 2.56q (4H, NCH_2CH$_3$, $^3J_{HH}$ 7.1 Hz), 3.77s (2H, CH_2N), 6.56 t (1H, C$_6$H$_4$, $^3J_{HH}$ 7.0 Hz), 6.68 t (1H, C$_6$H$_4$, $^3J_{HH}$ 7.0 Hz), 7.08dd (1H, C$_6$H$_4$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.5 Hz), 7.70dd (1H, C$_6$H$_4$, $^3J_{HH}$ 7.5, $^4J_{HH}$ = 1.5 Hz). ^{13}C (THF-d_8, 75.4 MHz): δ 12.03 (NCH$_2$CH_3), 47.60 (NCH_2CH$_3$), 61.47 (CH_2N), 120.52 (C$_5$), 125.21 (C$_4$), 128.68 (C$_3$), 139.33 (C$_6$), 142.28 (C$_2$), 144.74 (C$_1$).

4.4. Synthesis of [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Zn (3)

Elemental selenium (0.384 g, 4.86 mmol) was added to a solution of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li (0.686 g, 4.86 mmol) in 30 mL

anhydrous THF and the reaction mixture was stirred for 1 h at room temperature. All selenium powder was dissolved during this period. The resulted lithium selenolate solution was added dropwise under stirring to a cooled solution (−78 °C) of ZnCl$_2$ (0.33 g, 2.42 mmol) in 20 mL THF. The reaction mixture was left to reach room temperature and stirred overnight. The solvent was removed in vacuum and then the resulting solid was extracted with CH$_2$Cl$_2$. LiCl was filtered off and the clear solution was concentrated to approximately 2 mL. After treating with n-hexane 0.84 g (70.6%) of the title compound was isolated as a pale yellow solid. M.p. 209 °C. Anal. Found: C 43.73, H 4.81, N 5.98. Calc. for C$_{18}$H$_{24}$N$_2$Se$_2$Zn (M = 491.70): C 43.97, H 4.92, N 5.70%. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 1.67s (6H, NCH$_3$), 2.55s (6H, NCH$_3$), AB spin system with δ_A 3.14 and δ_B 4.07 (4H, CH$_2$N, $^2J_{HH}$ 11.2 Hz), 6.97d (2H, C$_6$H$_4$, H_4, $^3J_{HH}$ 7.3 Hz), 7.03 t (2H, C$_6$H$_4$, H_5, $^3J_{HH}$ 7.3 Hz), 7.05 t (2H, C$_6$H$_4$, H_3, $^3J_{HH}$ 7.5 Hz), 7.8d (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 7.3 Hz). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K): δ 1.03s (6H, NCH$_3$), 2.22s (6H, NCH$_3$), AB spin system with δ_A 2.50 and δ_B 3.89 (4H, CH$_2$N, $^2J_{HH}$ 11.2 Hz), 6.54d (2H, C$_6$H$_4$, H_4, $^3J_{HH}$ 7.2 Hz), 6.82 t (2H, C$_6$H$_4$, H_5, $^3J_{HH}$ 7.2 Hz), 6.87 t (2H, C$_6$H$_4$, H_3, $^3J_{HH}$ 7.4 Hz), 7.98d (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 7.4 Hz). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 328 K): δ 1.69s,br (12H, NCH$_3$), 3.20s,br (4H, CH$_2$N), 6.59d (2H, C$_6$H$_4$, H_4, $^3J_{HH}$ 7.3 Hz), 6.82 t (2H, C$_6$H$_4$, H_5, $^3J_{HH}$ 7.2 Hz), 6.88 t (2H, C$_6$H$_4$, H_3, $^3J_{HH}$ 7.5 Hz), 7.94d (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 7.5 Hz). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 45.75 (NCH$_3$), 49.54 (NCH$_3$), 68.82 (CH$_2$N), 124.34 (C$_5$), 128.92 (C$_3$), 130.98 (C$_4$), 135.44 (C$_2$), 137.22 (C$_6$), 137.26 (C$_1$). ^{77}Se (CDCl$_3$, 57.26 MHz): δ −81.2. MS (EI, 70 eV), m/z (%): 492 (98) [M$^+$], 477 (18) [M−Me$^+$], 278 (23) [2-(Me$_2$NCH$_2$)C$_6$H$_4$SeZn$^+$], 214 (67) [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se$^+$], 134 (100) [2-(Me$_2$NCH$_2$)C$_6$H$_4^+$]. ESI+ m/z (%): 770 (87) [{2-(Me$_2$NCH$_2$)C$_6$H$_4$Se}$_3$Zn$_2^+$], 515 (100) [M+Na]$^+$, 428 (67) [{2-(Me$_2$NCH$_2$)C$_6$H$_4$Se}$_2^+$].

4.4.1. [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Cd (4)

It was similarly prepared from elemental selenium (0.669 g, 8.47 mmol), [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li (1.195 g, 8.47 mmol) and CdCl$_2$ (0.776 g, 4.23 mmol). Yield 1.581 g (69.4%). M.p. 182 °C. Anal. Found:

C 39.82, H 4.52, N 5.32%. Calc. for $C_{18}H_{24}N_2Se_2Cd$ (M = 538.73): C 40.13, H 4.49, N 5.20%. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 1.99s,br (12H, NCH_3), 3.58s,br (4H, CH_2N), 6.99 m (6H, C$_6$H$_4$, H_{3-5}), 7.85d (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 7.2 Hz). ^{1}H NMR (CDCl$_3$, 300 MHz, 213 K): δ 1.25s (6H, NCH_3), 2.56s (6H, NCH_3), AB spin system with δ_A 2.88 and δ_B 4.22 (4H, CH_2N, $^2J_{HH}$ 11.4 Hz), 6.92d (2H, C$_6$H$_4$, H_4, $^3J_{HH}$ 6.8 Hz), 7.00 t (2H, C$_6$H$_4$, H_5, $^3J_{HH}$ 7.1 Hz), 7.08 t (2H, C$_6$H$_4$, H_3, $^3J_{HH}$ 7.3 Hz), 7.84d (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 7.2 Hz). ^{13}C (CDCl$_3$, 75.4 MHz): δ 46.64 (NCH_3), 67.51 (CH_2N), 124.70 (C_5), 128.62 (C_3), 131.66 (C_4), 133.84 (C_2), 137.88 (C_6,C_1). ^{77}Se (CDCl$_3$, 57.26 MHz): δ −111.5. ^{113}Cd (CDCl$_3$, 111 MHz): δ −196.2. MS (EI, 70 eV), m/z (%): 540 (23) [M$^+$], 214 (100) [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se$^+$], 134 (38) [2-(Me$_2$NCH$_2$)C$_6$H$_4^+$]. ESI+ m/z (%): 866 (43) [{2-(Me$_2$NCH$_2$)C$_6$H$_4$Se}$_3$Cd$_2^+$], 541 (38) [M+H]$^+$, 428 (100) [{2-(Me$_2$NCH$_2$)C$_6$H$_4$Se}$_2^+$].

4.5. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Zn (5)

To a mixture of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeNa (0.4 g, 1.51 mmol) and ZnCl$_2$ (0.102 g, 0.75 mmol) 15 mL of anhydrous THF was added and the reaction mixture was stirred for 24 h at 55 °C, under argon. The solvent was removed in vacuum and the obtained solid was treated with 30 mL toluene. NaCl was filtered off and from the clear solution the solvent was removed under reduced pressure. The brown solid residue was washed with 3 × 20 mL warm hexane (60 °C) to give the title compound as a white solid. Yield: 0.25 g (57.3%). M.p. 144−145 °C. Anal. Found: C 47.82.4, H 5.71, N 5.32%. Calc. for $C_{22}H_{32}N_2Se_2Zn$ (M = 547.81): C 48.24, H 5.89, N 5.11%. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 0.99s,br (12H, NCH$_2$CH_3), 2.81s,br (8H, NCH_2CH$_3$), 3.89s,br (4H, CH_2N), 6.99 m (4H, C$_6$H$_4$, $H_{4,5}$), 7.06 m (2H, C$_6$H$_4$, H_3), 7.67 m (2H, C$_6$H$_4$, H_6). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): δ 0.92 t (12H, NCH$_2$CH_3, $^3J_{HH}$ 7.1 Hz), 2.74q (8H, NCH_2CH$_3$, $^3J_{HH}$ 7.2 Hz), 3.81s,br (4H, CH_2N), 6.94 m (4H, C$_6$H$_4$, $H_{4,5}$), 7.02 m (2H, C$_6$H$_4$, H_3), 7.67 m (2H, C$_6$H$_4$, H_6). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 238 K): 0.55−1.66 (12H, NCH$_2$CH_3), 2.06−3.04 (8H, NCH_2CH$_3$), AB spin system with δ_A 3.56 and δ_B 4.18 (4H, CH_2N), 7.12 m (6H, C$_6$H$_4$, H_{3-5}), 7.63 m (2H, C$_6$H$_4$, H_6). ^{13}C (CDCl$_3$, 75.4 MHz): δ 9.06s,br (NCH$_2$CH_3), 46.60s,br (NCH_2CH$_3$), 62.99s,br (CH_2N), 124.01 (C_5), 128.53 (C_4), 131.19 (C_3), 135.92 (C_6), 136.85 (C_2), 137.83 (C_1). ^{77}Se (CDCl$_3$, 57.26 MHz): δ −59.02. ESI+ m/z (%): 854 (58) [{2-(Et$_2$NCH$_2$)C$_6$H$_4$Se}$_3$Zn$_2^+$], 549 (27) [M+H]$^+$, 485 (100) [{2-(Et$_2$NCH$_2$)C$_6$H$_4$Se}$_2^+$]

4.6. Synthesis of [2-(Et$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Cd (6)

To a solution of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]SeLi (0.55 g, 2.22 mmol) in 15 mL anhydrous THF was added CdCl$_2$ (0.203 g, 1.11 mmol) and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuum and the resulting solid was treated with 30 mL toluene. LiCl was filtered off and from the clear solution the solvent was removed under reduced pressure. The obtained glue was washed with 3 × 10 mL hexane to give the title compound as a yellowish solid. Yield: 0.45 g (68.3%). M.p. 127−128 °C. Anal. Found: C 44.84, H 5.52, 4.82%. Calc. for $C_{22}H_{32}N_2Se_2Cd$ (M = 594.84): C 44.42, H 5.42, N 4.71%. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 0.63s,br (12H, NCH$_2$CH_3), 2.61s,br (8H, NCH_2CH$_3$), 3.82s,br (4H, CH_2N), 6.97−7.02 m (6H, C$_6$H$_4$, H_{3-5}), 7.77d (2H, C$_6$H$_4$, H_6, $^3J_{HH}$ 7.6 Hz). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): 0.77s,br (NCH$_2$CH_3), 2.53s,br (8H, NCH_2CH$_3$), 3.75s,br (4H, CH_2N), 6.93 m (6H, C$_6$H$_4$, H_{3-5}), 7.66 m (2H, C$_6$H$_4$, H_6). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 223 K): δ −0.16s,br (6H, NCH$_2$CH_3), 1.08s,br (6H, NCH$_2$CH_3), 1.98s,br (4H, NCH_2CH$_3$), 2.92s,br (4H, NCH_2CH$_3$), AB spin system with δ_A 3.21 and δ_B 4.15 (4H, CH_2N, $^2J_{HH}$ 9.5 Hz), 6.88 m (6H, C$_6$H$_4$, H_{3-5}), 7.60 m (2H, C$_6$H$_4$, H_6). ^{13}C (CDCl$_3$, 75.4 MHz, 298 K): δ 9.65 (NCH$_2$CH_3), 47.74 (NCH_2CH$_3$), 61.41 (CH_2N), 124.53 (C_5), 128.55 (C_4), 132.04 (C_3), 134.89 (C_6), 137.10 (C_2), 137.81 (C_1). ^{77}Se (CDCl$_3$, 57.26 MHz):

δ −94.97. ESI+ m/z (%): 948 (84) [{2-(Et$_2$NCH$_2$)C$_6$H$_4$Se}$_3$Cd$_2^+$], 597 (48) [M]$^+$, 485 (100) [{2-(Et$_2$NCH$_2$)C$_6$H$_4$Se}$_2^+$].

4.7. X-ray structure determination

Block crystals of [2-(Et$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (1), [2-(Me$_2$NCH$_2$) C$_6$H$_4$Se]$_2$Zn (3) and [2-(Me$_2$NCH$_2$)C$_6$H$_4$Se]$_2$Cd (4) were attached with Paratone N oil on cryoloops. The data were collected at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The details of the crystal structure determination and refinement are given in Table 2.

The structures were refined with anisotropic thermal parameters. The 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 [41]. The drawings were created with the Diamond program [42].

Appendix A. Supplementary data

CCDC 753670, 753676 and 753671 contain the supplementary crystallographic data for compounds 1, 3 and 4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The supplementary material also contains figures representing the supramolecular associations in the crystals of compounds 3 and 4.

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.07.036.

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