

*Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary*

NEW DIORGANOCHALCOGEN COMPOUNDS BASED ON THE 2-(Me₂NCH₂)C₆H₄ GROUP

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ABSTRACT. Heteroleptic diorganochalcogen compounds of type R[2-(Me₂NCH₂)C₆H₄]E [R = (phtz)CH₂, E = Se (**1**), S (**2**); R = (4-Cl-phtz)CH₂, E = S (**3**); R = (pz)CH₂CH₂, E = Se (**4**)] were prepared by reacting 2-(Me₂NCH₂)C₆H₄ELi with the appropriate organic halide in a 1:1 molar ratio. The new compounds were investigated in solution by ¹H, ¹³C and ⁷⁷Se NMR where appropriate. For compounds **1** and **4** the crystal and molecular structures were determined by single-crystal X-ray diffraction.

Keywords: *Diorganoselenium compounds, hypercoordination, structure elucidation*

INTRODUCTION

The organoselenium compounds bearing organic groups with possibilities of O→Se or N→Se intramolecular coordination attracted a considerable increased interest during last years due to their improved hydrolytic and thermal stability [1-3]. They are well-known active species in different organic transformations, *i.e.* selective hydrogenation, methoxyse-lenylation or selenocyclization [4-7], or as enzyme models and chemotherapeutic reagents [8-10]. A special interest attracted their use as neutral or anionic ligands towards main group or *d* metals, such metal complexes being valuable candidates as single-source precursors for metal selenides [11].

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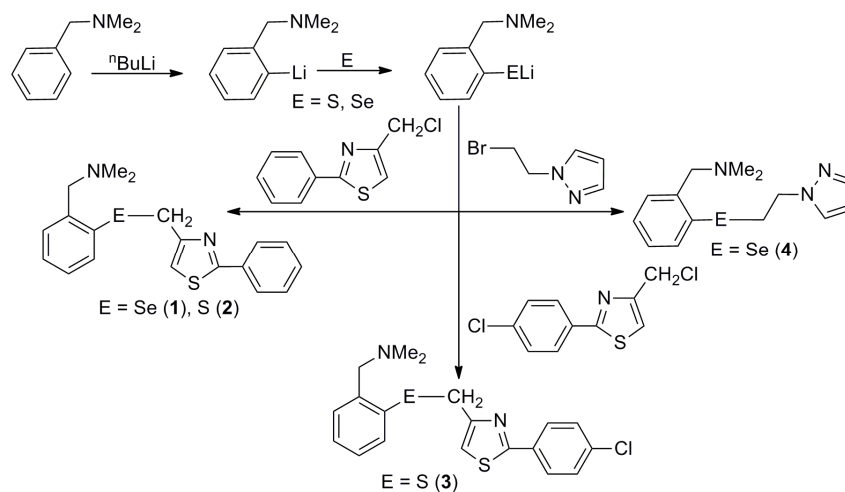
On the other hand, pyrazole or thiazole based compounds proved to have a significant importance in medicinal chemistry, as anti-inflammatory, antibacterial or antitumor agents [12-16].

During last years our studies were focused on organoselenium compounds of type Ar_2Se_2 , ArSeX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) or ArSeL ($\text{L} = \text{organophosphorus ligand}$) bearing organic groups (Ar) with one or two pendant arms, *i.e.* $2\text{-(R}_2\text{NCH}_2\text{)C}_6\text{H}_4$ and $2,6\text{-(R}_2\text{NCH}_2\text{)}_2\text{C}_6\text{H}_3$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$, $\text{R}_2 = (\text{CH}_2\text{CH}_2)_2\text{O}, (\text{CH}_2\text{CH}_2)_2\text{NMe}$ [17-20], as well as their metal complexes [21,22]. Recently we reported about the compounds $[2\text{-(R}_2\text{NCH}_2\text{)C}_6\text{H}_4][(\text{3,5-dmpz})\text{CH}_2\text{CH}_2\text{]Se}$, [$\text{R} = \text{Me}, \text{Et}$, $\text{dmpz} = \text{dimethylpyrazole}$] and their behavior towards gold, silver and palladium [23]. As a continuation of our studies we report here about the synthesis and structural characterization of the new diorganoselenium compounds $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4][(\text{pz})\text{CH}_2\text{CH}_2\text{]Se}$ ($\text{pz} = \text{pyrazole}$) and $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4][(\text{phtz})\text{CH}_2\text{]Se}$ ($\text{phtz} = \text{phenylthiazole}$), as well as the related sulfur containing compounds $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4][(\text{phtz})\text{CH}_2\text{]S}$ and $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4][(\text{4-Cl-phtz})\text{CH}_2\text{]S}$.

RESULTS AND DISCUSSION

Synthesis and spectroscopy

Several diorganochalcogen compounds containing the $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$ group with potential for $\text{N} \rightarrow \text{E}$ intramolecular interactions were prepared by reacting the lithiated derivative $\text{LiEC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ ($\text{E} = \text{S}, \text{Se}$) with the appropriate organic halide in a 1:1 molar ratio, as depicted in Scheme 1.



The new compounds were isolated as solid species, soluble in common organic solvents. They were characterized by solution multinuclear NMR (¹H, ¹³C and ⁷⁷Se where appropriate).

The ¹H and ¹³C NMR spectra show the expected resonances for the organic groups. The resonances corresponding to the aromatic protons in all compounds appear as multiplets, due to the proton – proton couplings. The protons in the CH₂ and the NMe₂ groups in the pendant arm of the 2-(Me₂NCH₂)C₆H₄ ligands appear as singlet, thus giving no information about a possible N→E interaction in solution.

The ⁷⁷Se NMR spectra of compounds **1** and **4** present singlet resonances at δ values of 315.28 and 241.1 ppm, respectively.

Single-crystal X-ray diffraction studies

For compounds **1** and **4** the molecular structures were determined by single-crystal X-ray diffraction. The two compounds have similar molecular structures. The Ortep-like diagrams with the atom numbering schemes for compounds **1** and **4** are given in Figures 1 and 2, respectively, while important interatomic distances and angles are given in Table 1.

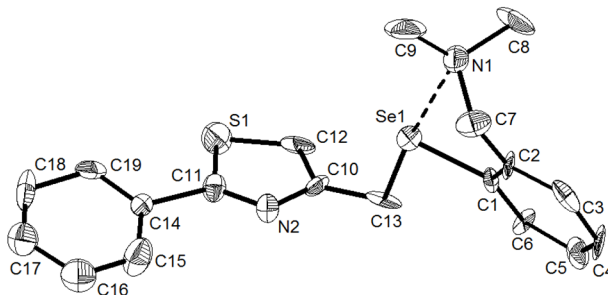


Figure 1. Ortep-like diagram with 30% probability ellipsoids of *R*_{N1}-**1**. Hydrogen atoms are omitted for clarity.

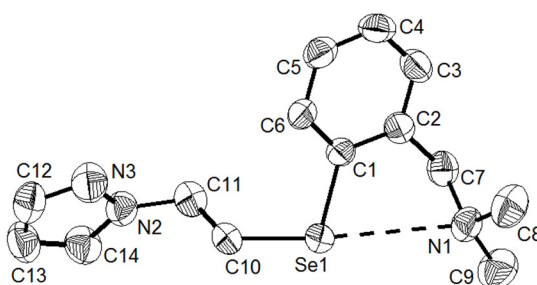


Figure 2. Ortep-like diagram with 50% probability ellipsoids of *R*_{N1}-**4**. Hydrogen atoms are omitted for clarity.

In both compounds a T-shaped coordination geometry is realized around selenium. The 2-(Me₂NCH₂)C₆H₄ group acts as a C,N chelating ligand, while the thiazole group in **1** and the pyrazole group in **4** are not involved in any interaction with selenium.

Table 1. Important interatomic distances (Å) and angles (deg.) in **1** and **4**

1		4	
C1–Se1	1.926(3)	C1–Se1	1.923(3)
C13–Se1	1.983(3)	C10–Se1	1.957(4)
N1–Se1	2.836(3)	N1–Se1	3.093(3)
C1–Se1–C13	99.59(14)	C1–Se1–C10	101.7(2)
N1–Se1–C13	173.15(12)	N1–Se1–C10	172.99(1)
N1–Se1–C1	73.75(11)	C1–Se1–N1	72.05(9)

The N→Se intramolecular interaction is longer in compound **4** than in **1**, but much shorter than the sum of the van der Waals radii of the two elements ($\Sigma r_{vdW}(N,Se)$ 3.54 Å [24]). The five-membered SeC₃N rings are not planar, but folded along the imaginary axes Se1⋯C7. Moreover, the N→Se intramolecular interaction induces planar chirality and, as a consequence, the respective compounds crystallize as 1:1 mixtures of *R* and *S* isomers.

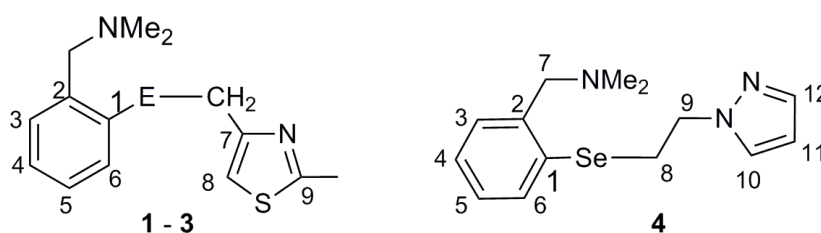
CONCLUSIONS

Our studies revealed a C,N bidentate behavior of the 2-(Me₂NCH₂)C₆H₄ group in compounds **1** and **4** in solid state. The room temperature NMR spectra suggest either the absence of the N→E (E = S, Se) intramolecular interaction in solution, or a dynamic behavior involving de-coordination, inversion at nitrogen and re-coordination to chalcogen, too fast to be observed at the NMR time scale.

EXPERIMENTAL SECTION

Starting materials, *i.e.* 2-(Me₂NCH₂)C₆H₄ELi [25], pzCH₂CH₂Br [26], (phtz)CH₂Cl and (4-Cl-phtz)CH₂Cl [27] were prepared according to literature procedures. ⁿBuLi and other starting chemicals were commercially available. All manipulations involving air sensitive compounds were carried out under argon, using Schlenk techniques. Solvents were dried and distilled prior to use. Elemental analyses were performed on a Flash EA 1112 machine. Melting points have been determined with an ELECTROTHERMAL 9200 apparatus and they are not corrected. Multinuclear NMR spectra (¹H, ¹³C and ⁷⁷Se) were

recorded on a BRUKER 400 instrument operating at 400.1, 100.6 and 76.3 MHz, respectively, using CDCl₃ solutions. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CHCl₃: ¹H 7.26, ¹³C 77.0 ppm) and Me₂Se, respectively. The ¹H and ¹³C chemical shifts were assigned based on 2D experiments (COSY, HSQC and HMBC) using standard BRUKER XWIN-NMR pulse sequences and they are given according to the numbering in Scheme 2. The NMR spectra were processed using the MestReC and MestReNova software [28].



Scheme 2.

Preparation of *N,N*-dimethyl-1-(2-((2-phenylthiazol-4-yl)methyl)phenyl)metanamine (1)

Selenium powder (0.347 g, 4.4 mmol) was added to a solution of 2-Me₂NCH₂C₆H₄Li (0.62 g, 4.4 mmol) in THF (30 mL) at room temperature and stirring was continued for 2 hours. To the as obtained lithium organoselenolate a solution of 4-(chloromethyl)-2-phenylthiazol (0.92 g, 4.4 mmol) in THF (20 ml) was added dropwise and the reaction mixture was stirred over night. Then the solvent was removed under reduced pressure and the remained solid was treated with toluene. The precipitated LiCl was filtered off and toluene was removed under reduced pressure, when the title compound resulted as a colourless powder. Yield 1.3 g (76%) M.p. 91°C. Anal. Calc. for C₁₉H₂₀N₂S₂Se (M = 387.40) C 58.91, H 5.20, N 7.23%. Found: C 58.83, H 5.22, N 7.31%. ¹H NMR: δ 2.21 (s, 6H, NCH₃); 3.46 (s, 2H, NCH₂); 4.26 (s, 2H, SeCH₂); 6.98 (s, 1H, H₈); 7.18 – 7.27 (m, 3H, C₆H₄); 7.43 (m, 3H, C₆H₅-meta+para); 7.62 (m, 1H, C₆H₄); 7.89 – 7.97 (m, 2H, C₆H₅-ortho); ¹³C NMR: δ 26.05 (s, SeCH₂, ¹J_{SeC} 17.2 Hz), 44.77 (s, NCH₃), 64.47 (s, NCH₂), 115.06 (C₈), 126.16 (C₆H₄), 126.57 (C₆H₅-ortho), 127.77 (C₆H₄), 128.89 (C₆H₅-meta), 129.62 (C₆H₄), 129.96 (C₆H₅-para), 131.63 (C₆H₄), 133.66 (C₈), 134.00 (C₁), 140.41 (C₂), 154.88 (C₇), 167.88 (C₆H₅-ipso). ⁷⁷Se NMR: δ 315.28s

Preparation of *N,N*-dimethyl-1-(2-(((2-phenylthiazol-4-yl)methyl)thio)phenyl) metanamine (2)

Sulfur powder (0.138 g, 4.3 mmol) was added to a solution of 2-Me₂NCH₂C₆H₄Li (0.61 g, 4.3 mmol) in THF (30 mL) at room temperature and stirring was continued for 2 hours. To the as obtained lithium organothiolate a solution of 4-(chloromethyl)-2-phenylthiazol (0.90 g, 4.3 mmol) in THF (20 ml) was added dropwise and the reaction mixture was stirred over night. Then the solvent was removed under reduced pressure and the remained oil was treated with toluene. The precipitated LiCl was filtered off, and toluene was removed under reduced pressure, when the title compound resulted as an orange powder. Yield 1.34 g (92%) M.p. 95°C. Anal. Calc. for C₁₉H₂₀N₂S₂ (M = 340.51) C 67.02, H 5.92, N 8.23%. Found: C 67.22, H 6.07, N 8.34%. ¹H NMR: δ 2.26 (s, 6H, NCH₃); 3.51 (s, 2H, NCH₂); 4.31 (s, 2H, SCH₂); 7.01 (s, 1H, H₈); 7.11 – 7.22 (m, 2H, C₆H₄); 7.21 (d, 1H, C₆H₄, ³J_{HH} 7.3 Hz); 7.39 (d, 1H, C₆H₄, ³J_{HH} 7.5 Hz); 7.40 – 7.48 (m, 3H, C₆H₅-meta+para); 7.92 – 7.94 (m, 2H, C₆H₅-ortho); ¹³C NMR: δ 34.29 (SCH₂), 45.34 (NCH₃), 62.02 (NCH₂), 115.76 (C₈), 125.94 (C₆H₄), 126.56 (C₆H₅-ortho), 127.65 (C₆H₄), 128.94 (C₆H₅-meta), 129.29 (C₆H₄), 129.99 (C₆H₅-para), 130.06 (C₆H₄), 133.54 (C₈), 136.30 (C₁), 138.95 (C₂), 153.80 (C₇), 168.17 (C₆H₅-ipso).

Preparation of 1-(2-(((2-(4-chlorophenyl)thiazol-4-yl)methyl)thio)phenyl)-*N,N*-dimethylmethanamine (3)

To a solution of 2-Me₂NCH₂C₆H₄SLi (0.63 g, 3.6 mmol) in THF (30 mL) was added a solution of 4-(chloromethyl)-2-(4-chlorophenyl)thiazol (0.88 g, 3.6 mmol) in THF (20 ml). and the reaction mixture was stirred over night. Then the solvent was removed under reduced pressure and the remained orange oil was treated with toluene. The precipitated LiCl was filtered off, and toluene was removed under reduced pressure. The remained orange oil was treated with n-hexane, when the title compound precipitated as an orange powder. Yield 1.31 g (97%) M.p. 80°C. Anal. Calc. for C₁₉H₁₉ClN₂S₂ (M = 374.95) C 60.86, H 5.11, N 7.47%. Found: C 60.73, H 5.21, N 7.51%. ¹H NMR: δ 2.20 (s, 6H, NCH₃); 3.47 (s, 2H, NCH₂); 4.37 (s, 2H, SCH₂); 6.56 (s, 1H, H₈); 7.18 – 7.24 (m, 2H, C₆H₄); 7.31 – 7.35 (m, 2H, C₆H₄); 7.43 (d, 2H, C₆H₅- meta, ³J_{HH} 7.9 Hz); 8.12 (d, 2H, C₆H₅- ortho, ³J_{HH} 8.1 Hz); ¹³C NMR: δ 30.36 (SCH₂), 45.19 (NCH₃), 62.58 (NCH₂), 109.68 (C₈), 127.30 (C₆H₄), 127.93 (C₆H₄), 128.04 (4-ClC₆H₄-ortho), 128.90 (4-ClC₆H₄-meta), 129.75 (C₆H₄), 129.97 (C₆H₄), 130.56 (4-ClC₆H₄-para), 131.54 (C₈), 134.66 (C₁), 135.61 (C₂), 157.04 (C₇), 166.11 (4-ClC₆H₄-ipso).

Preparation of 1-(2-((2-(1H-pyrazol-1-yl)ethyl)selenyl)phenyl)-N,N-dimethyl-methanamine (4)

Selenium powder (0.68 g, 8.5 mmol) was added to a solution of 2-Me₂NCH₂C₆H₄Li (1.20 g, 8.5 mmol) in THF (25 mL) and the reaction mixture was stirred under argon for 3 hours. Then a solution of 1-(2-bromoethyl)pyrazol (1.49 g, 8.5 mmol) in THF (10 mL) was added dropwise and the reaction mixture was stirred over night. Then the solvent was removed under reduced pressure and the remained solid was treated with toluene. The precipitated LiCl was filtered off, and toluene was removed under reduced pressure. The remained solid was washed with n-hexane and the title compound resulted as a yellow solid. Yield: 2.38 g (91%) M.p. 45°C. Anal. Calc. for C₁₄H₁₉N₃Se (M = 308.28) C 54.54, H 6.21, N 13.63%. Found: C 54.22, H 6.51, N 13.78%. ¹H NMR: δ 2.23 (s, 6H, NCH₃), 3.31 (t, 2H, H₈, ³J_{HH} 7.33 Hz), 3.48 (s, 2H, H₇), 4.40 (t, 2H, H₉, ³J_{HH} 7.44 Hz), 6.24 (s, 1H, H₁₁), 7.21 (m, 2H, C₆H₄), 7.28 (d, 1H, C₆H₄, ³J_{HH} 7.14 Hz), 7.38 (s, 1H, H₁₂), 7.48 (d, 1H, C₆H₄, ³J_{HH} 7.27 Hz), 7.55 (s, 1H, H₁₀). ¹³C NMR: δ 26.04 (C₅), 44.86 (NCH₃), 52.15 (C₇), 64.66 (C₄), 105.47 (C₁₁), 126.31 (C₆H₄), 128.12 (C₆H₄), 129.32 (C₆H₄), 130.11 (C₁₀), 130.81 (C₁₂), 132.31 (C₆H₄), 139.79 (C₆H₄), 140.63 (C₆H₄). ⁷⁷Se NMR: δ 241.1s, broad.

X-ray Crystallographic Studies

X-ray quality crystals of compounds **1** and **4** resulted by slow diffusion from a mixture of CDCl₃ and n-hexane (1/4, v/v). The crystals were attached with paraton/N oil to cryoloops. Data collection and processing were carried on a Bruker SMART APEX CCD system, using graphite-monochromated Mo K α radiation. Details of the crystal structure determination and refinement are given in Table 2.

Table 2. Crystallographic data for compounds **1** and **4**.

	1	4
Empirical formula	C ₁₉ H ₂₀ N ₂ SSe	C ₁₄ H ₁₉ N ₃ Se
Formula weight	387.39	308.28
Temperature, K	297(2)	297(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	monoclinic
Space group	P -1	P2(1)/n
Crystal size, mm	0.40 x 0.33 x 0.30	0.40 x 0.32 x 0.28
Unit cell dimensions		
a, Å	6.101(4)	11.797(3)
b, Å	11.062(7)	5.3923(15)
c, Å	14.045(8)	23.848(7)

	1	4
α , °	79.694(10)	90.00
β , °	86.408(9)	103.299(5)
γ , °	81.020(9)	90.00
V, Å ³	920.6(9)	1476.4(7)
Z, Calculated density	2, 1.397 mg/m ³	4, 1.387 mg/m ³
F(000)	396	632
Refinement method	Full-matrix least-squares on F ²	
Θ Range for data collection, deg.	1.475 to 24.999	1.75 to 25.00
Reflections collected	8572	13300
Independent reflections [R _{int}]	3202 R(int) = 0.0447	2599, R(int) = 0.0432
Data/restraints/parameters	3202 / 0 / 208	2599 / 0 / 165
Goodness-of-fit on F ²	1.022	1.056
Final R indices [I > 2 σ (I)]	R1 = 0.0407, wR2 = 0.0864	R1 = 0.0445, wR2 = 0.1061
R indices (all data)	R1 = 0.0531, wR2 = 0.0907	R1 = 0.0543, wR2 = 0.1102
Largest diff. peak and hole, (e Å ⁻³)	0.502 and -0.303	0.846 and -0.560

The structure was refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. The software package SHELX-97 was used for structure solving and refinement [29]. The drawings were created with the DIAMOND program [30].

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SUPPLEMENTARY DATA

CCDC 1477916 and 1477915 contain the supplementary crystallographic data for **1** and **4**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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