Journal of Fluorine Chemistry 144 (2012) 118–123

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

New polyfluorinated aromatic and aza-aromatic diselenides, selenyl chlorides, non-symmetric selenides and selenoxides

Arkady G. Makarov, Alexander Yu. Makarov, Irina Yu. Bagryanskaya, Makhmut M. Shakirov, Andrey V. Zibarev *

Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia

ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form 14 August 2012
Accepted 16 August 2012
Available online 23 August 2012

Keywords:
Aza-aromatics
Aromatics
Diselenides
Organofluorine
Selenides
Selenoxides
Selenyl chlorides
Synthesis

ABSTRACT

New polyfluorinated Ar–Se–Se–Ar, Ar–Se–Cl (Ar = 4-RC_6F_4-1-yl, 5-HC_5F_3N-3-yl), non-symmetric Ar–Se–Ar′ (Ar = 4-RC_6F_4-1-yl, Ar′ = 4-NC_5F_4-1-yl) and non-symmetric, *i.e.* chiral, Ar–Se(=O)–Ar′ (Ar = Ar = 4-RC_6F_4-1-yl, Ar′ = 4-NC_5F_4-1-yl) derivatives, as well as (4-NC_5F_4-1-yl)SeNa, were prepared and characterized by single-crystal X-ray diffraction and multinuclear NMR (^{1}H, ^{13}C, ^{14}N, ^{19}F, ^{77}Se).

1. Introduction

Aromatic selenium compounds, particularly diselenides, selenyl chlorides, selenolates and selenoxides, are versatile reagents in organic, organoelement and main group chemistry [1,2]. Their polyfluorinated congeners, especially non-symmetric (where possible), are studied to much lesser extent [3,4]. At the same time they are of interest to fundamental chemistry [1–5] and its applications to the materials science [5–9].

In this work we report on preparation and characterization of new polyfluorinated Ar–Se–Se–Ar, Ar–Se–Cl (Ar = 4-RC_6F_4-1-yl, 5-HC_5F_3N-3-yl), non-symmetric Ar–Se–Ar′ (Ar = 4-RC_6F_4-1-yl, Ar′ = 4-NC_5F_4-1-yl) and non-symmetric, *i.e.* chiral, Ar–Se(=O)–Ar′ (Ar = 4-RC_6F_4-1-yl, Ar′ = 4-NC_5F_4-1-yl) derivatives, as well as selenolate (4-NC_5F_4-1-yl)SeNa (Chart 1). The compounds synthesized were characterized by multinuclear (^{1}H, ^{13}C, ^{14}N, ^{19}F, ^{77}Se) NMR, and compounds **3**, **5**, **9**, **12** and **14** by single-crystal X-ray diffraction (XRD).

2. Results and discussion

The diselenides **1**–**5** were obtained from corresponding arenes by three-step one-pot procedure (Scheme 1). The isolated yields varied from 24% (**5**) to 77% (**3**). The structures of **3** and **5** were confirmed by XRD (Fig. 1; Supporting Information, Fig. S1).

The selenyl chlorides **6**–**9** were synthesized from the corresponding diselenides **1**, **2**, **4** and **5** in practically quantitative isolated yields by the action of elemental chlorine (Scheme 2). The structure of compound **9** was confirmed by XRD (Fig. 2; Supporting Information, Fig. S2). Diselenide **3** under action of either chlorine or SO_2Cl_2 produced only complex mixture of unidentified compounds. In the context of compounds **4**, **5**, **8** and **9**, it should be noted that they represent rather rare functional derivatives of 2,3,4,6-tetrafluoropyridine [10], furthermore first Se-containing derivatives.

Polyfluorinated diselenides are suitable precursors of corresponding selenolates which are useful reagents and ligands [5]. Attempt of reduction of C_6F_5–Se–Se–C_6F_5 (**15**) with Ph_3P/H_2O in pyridine (the method is known to perform well for C_6H_5–X–X–C_6H_5, X = Se, S [11]) was unsuccessful, only Ph_3P = Se (identified by XRD in full agreement with previous results [12]) and a mixture of unidentified products were isolated. Reduction of **1** and **15** with $NaBH_4$ allowed however preparing of corresponding selenolates trapped by pentafluoropyridine to give non-symmetric selenides

---

* Corresponding author. Fax: +7 383 330 9752.
E-mail address: zibarev@nioch.nsc.ru (A.V. Zibarev).

0022-1139/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2012.08.002

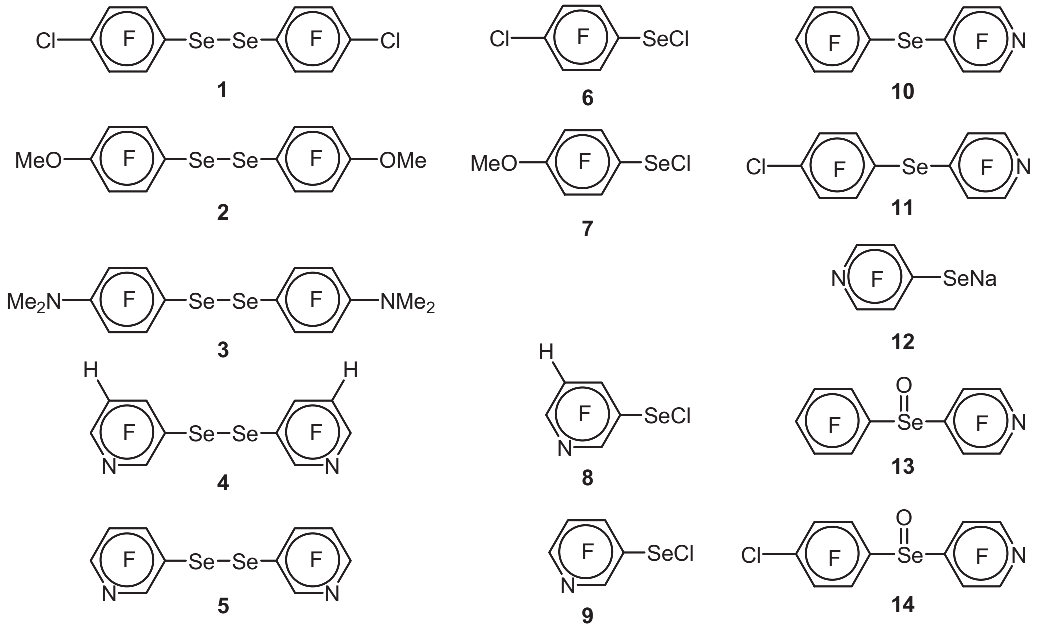
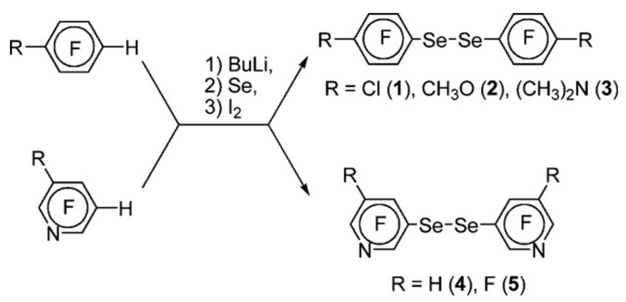


Chart 1. Compounds synthesized.



Scheme 1. Synthesis of the diselenides **1**–**5**.

10 and **11** in the isolated yields of 42 and 85%, respectively (Scheme 3). From the preparation of compound **10**, selenolate (4-NC$_5$F$_4$-1-yl)SeNa (**12**) was unexpectedly isolated as minor by-product identified by XRD in the form of **12**·3H$_2$O after crystallization from wet acetone (Fig. 3).

The selenides **10** and **11** were converted to non-symmetric, *i.e.* chiral, selenoxides **13** and **14** by oxidation with KMnO$_4$ in acetic acid with isolated yields of 39 and 77%, respectively (Scheme 4). Other oxidizers tried including 3-chloroperbenzoic acid (*cf.* [13]), H$_2$O$_2$ (30%) and HNO$_3$ (100%) were not effective Fig. 4.

Molecular and crystal structures of compound **14** confirmed by XRD (Fig. 3; Supporting Information, Fig. S3) are very similar to those of C$_6$F$_5$Se(=O)C$_6$F$_5$ [13].

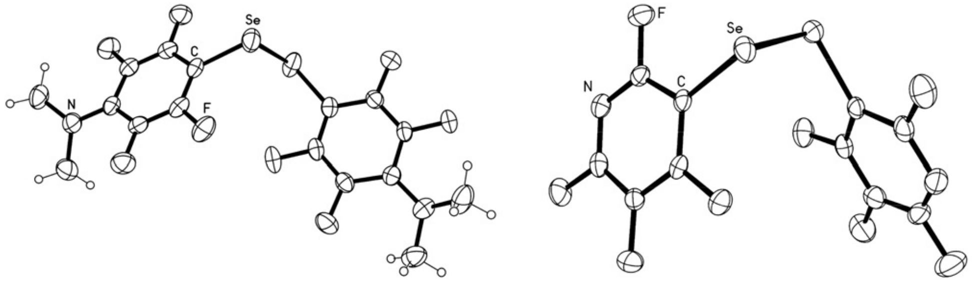
3. Conclusions

Synthetic protocols for preparation of new polyfluorinated aromatic and aza-aromatic Ar–Se–Se–Ar, Ar–Se–Cl (Ar = 4-RC$_6$F$_4$-1-yl, 5-HC$_5$F$_3$N-3-yl), non-symmetric Ar–Se–Ar′ (Ar = 4-RC$_6$F$_4$-1-yl, Ar′ = 4-NC$_5$F$_4$-1-yl) and non-symmetric, *i.e.* chiral, Ar–Se(=O)–Ar′ (Ar = 4-RC$_6$F$_4$-1-yl, Ar′ = 4-NC$_5$F$_4$-1-yl) derivatives are elaborated. Compounds **4**, **5**, **8** and **9** represent first Se-containing derivatives of 2,3,4,6-tetrafluoropyridine. The compounds synthesized can be used as reagents and ligands in organoelement, main group and coordination chemistry.

4. Experimental

4.1. General

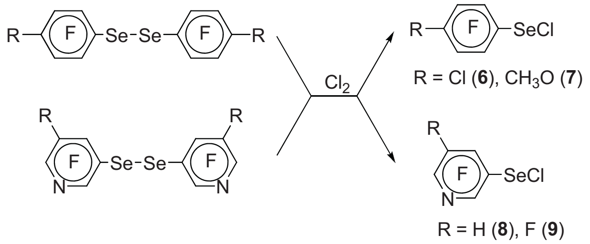
The ^{1}H, ^{13}C, ^{14}N and ^{77}Se NMR spectra were measured with a Bruker AV-600 spectrometer at the frequencies of 600.1, 151.0, 43.4 and 114.5 MHz, respectively, and the ^{19}F NMR spectra with a Bruker AV-300 spectrometer at the frequency of 282.4 MHz, for



3

5

Fig. 1. XRD molecular structures of compounds **3** and **5** (displacement ellipsoids at 30%). Selected bond lengths (Å), bond and torsion angles (°): Compound **3**: C–Se 1.899(5) and 1.907(5), Se–Se 2.3385(12); C–Se–Se 101.8(2) and 100.45(19); C–Se–Se–C −106.52. Compound **5**: C–Se 1.914(4) and 1.911(4), Se–Se 2.3192(8); C–Se–Se 99.71(12) and 100.13(12); C–Se–Se–C −79.44(17).



Scheme 2. Synthesis of the selenyl chlorides **6–9**.

solutions in $CDCl_3$ unless otherwise indicated. Chemical shifts (δ) are given with respect to TMS (^1H, ^{13}C), NH_3 (liq.) (^{14}N), C_6F_6 (^{19}F), and $Se(CH_3)_2$ (^{77}Se).

High-resolution mass spectra (EI, eV) of compounds **1–5**, **10** and **11** were taken with a Termo Scientific DFS mass spectrometer with direct inlet and source temperature 160 °C. Electrospray ionization (ESI) mass spectra of compounds **13** and **14** were obtained with a Bruker Daltonik micrOTOF-Q hybrid quadrupole time-of-flight mass-spectrometer equipped with electrospray ionization source, for MeOH solutions, with nitrogen as drying gas. ESI-MS conditions: positive scan in the range $m/z = 80–3000$, $V_{cap} = 4500$ V, drying gas flow and temperature 4.0 L/min and 190 °C, nebylizer pressure 1.0 bar. A small syringe pump was used for the introduction of solution samples directly to spray chamber of the mass-spectrometer, flow rate was 2 μL/min. For selenyl chlorides **6–9** mass spectra were not obtained due to instability of the compounds under MS conditions.

UV–vis spectra were recorded with HP 8453 spectrophotometer for heptane solutions.

The solvents were dried with common drying agents. The reaction solvents were distilled off under reduces pressure.

Starting 2,3,5,6-tetrafluoro-1-chlorobenzene [14], 2,3,5,6-tetrafluoroanisole [15], N,N-dimethyl-2,3,5,6-tetrafluoroaniline [16], 2,4,6-trifluoropyridine and 2,3,4,6-tetrafluoropyridine [17], and pentafluoropyridine [18] were described before.

Tables 1–4 contain NMR, XRD, physical, spectral and analytical data of the compounds synthesized.

4.2. X-ray diffraction

The XRD data for **3**, **5** and **9** were collected on a Bruker P4 diffractometer with $\theta/2\theta$ scans, and for **12** and **14** on a Bruker Kappa Apex II CCD diffractometer with φ, ω scans of narrow (0.5°) frames, using Mo Kα (λ = 0.71073 Å) radiation with a graphite monochromator. Absorption corrections for **5** were applied by integration taking into account real crystal shape; those for **3** and **9** were applied by empirical methods based on ψ scans, and for **12** and **14** using the *SADABS* program. The structures were solved by direct methods using the *SHELXS-97* program and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation using the *SHELXL-97* program [19]. The H atoms positions for **3** were calculated with the riding model and for **12** located from difference Fourier map. The obtained structures were analyzed with the *PLATON* [20] and *MERCURY* [21] programs.

Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Center as CCDC-891650 (**3**), –891651 (**5**), –891652 (**9**), –891653 (**12**) and –891654 (**14**).

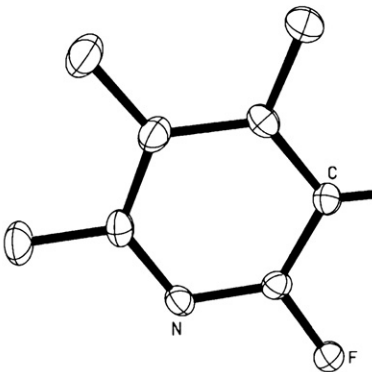


Fig. 2. XRD molecular structure of compound **9** (displacement ellipsoids at 30%). Selected bond lengths (Å), bond and torsion angles (°) (two crystallographically independent molecules): C–Se 1.904(4) (in both molecules), Se–Cl 2.1877(11) and 2.1859(11); C–Se–Cl 95.85(11) and 95.47(11); (N–)C–C–Se–Cl 114.9(3) and 117.5(3).

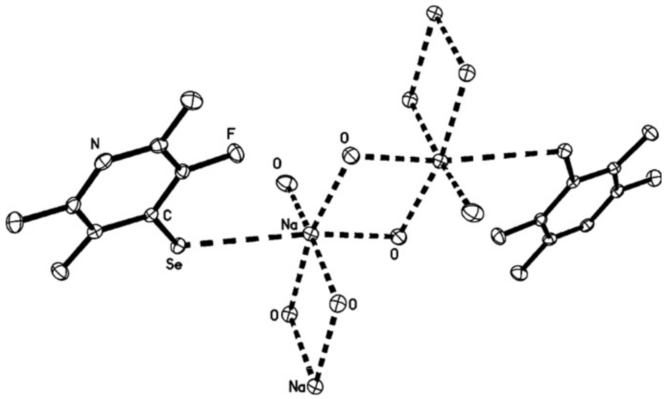
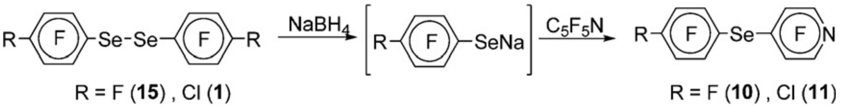


Fig. 3. XRD molecular structure of **12**·$3H_2O$ (displacement ellipsoids at 30%). Selected bond lengths (Å) and bond angles (°): C–Se 1.8853(16), Se•Na 3.2068(9), Na••O 2.3957(16), 2.4123(17), 2.4010(17), 2.4646(15) and 2.3344(19); C–Se–Na 114.51(5).

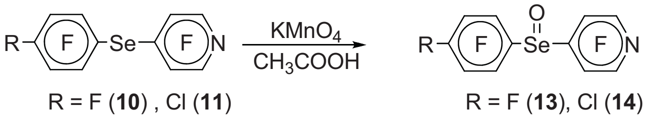
4.3. Preparations

4.3.1. Diselenides **1–5**

At −60 °C and under argon, 40 mmol of *n*-BuLi (2.5 M solution in hexanes) was added dropwise to a stirred solution of 40 mmol of corresponding (aza)arene in 100 ml of Et_2O. After additional 30 min., 3.16 g (40 mmol) of finely ground elemental Se was added by small portions. After additional 2 h, the reaction mixture was slowly warmed to −55 (**4**), −30 (**5**), or −10 °C (**1–3**), and 5.08 g (20 mmol) of elemental iodine was added. After additional 30 min., the reaction mixture was warmed to ambient temperature and excess of aqueous $Na_2S_2O_3$ was slowly added. The organic and water layers were separated, and the latter was extracted with Et_2O (**2–4**) or $CHCl_3$ (**1**). Combined organic solution was dried with $MgSO_4$, filtered and evaporated. The residue was crystallized from hexane (**1–3**, **5**) or its 2:1 mixture with chloroform (**4**). In the case of **1** and **5**, chromatography on silica column was employed before crystallization, eluent hexane/benzene 20:1. Compounds **2** and **5** were additionally purified by sublimation at 140 °C/8 mm and 80 °C/2 mm, respectively. Compounds **1**, **2**, **4**, **5** were obtained in



Scheme 3. Synthesis of compounds **10** and **11**.



Scheme 4. Synthesis of compounds **13** and **14**.

the form of yellow prisms or needles, and compound **3** in the form of red needles.

4.3.2. Selenyl chlorides *6–9*

At ambient temperature, excess of elemental chlorine was slowly passed through stirred solution of 1 mmol of corresponding diselenide (**1**, **2**, **4**, **5**) in 10 ml of CCl_4. The solvent was distilled off. Compounds **6–9** were obtained in the form of dark-red oil, which in the case of compounds **8** and **9** crystallized below 4 °C in deep-red plates.

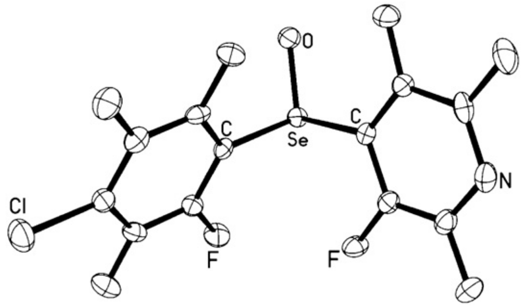


Fig. 4. XRD molecular structure of compound **14** (displacement ellipsoids at 30%). Selected bond lengths (Å) and bond angles (°) (three crystallographically independent molecules): C–Se 1.975(9) and 1.966(8), 1.967(9) and 1.953(8), 1.964(10) and 1.974(9), Se–O 1.647(7), 1.645(7) and 1.656(7); C–Se–O 104.7(4) and 105.0(3), 104.8(4) and 104.3(4), 101.8(4) and 104.5(4), C–Se–C 92.3(4), 95.7(4) and 96.2(4).

Table 1
NMR chemical shifts, δ, for compounds.[a]

	^{13}C	^{19}F	^{77}Se
1	147.0, 143.6, 115.2, 106.8	36.8, 23.2	377
2	147.5, 140.6, 140.2, 100.3, 62.0	34.3, 5.6	367
3	147.7, 140.7, 133.5, 97.0, 42.8	32.8, 11.1	371
4	173.2, 163.6, 162.4, 97.5, 95.9	107.0, 100.5, 82.8	352
5	160.2, 155.1, 151.2, 132.8, 98.8	102.9, 81.6, 62.1, −1.6	372
6	146.5, 143.8, 117.5, 107.9	39.4, 24.0	809
7	147.3, 142.7, 140.0, 101.2, 61.9	37.2, 6.0	809
8	173.0, 165.0, 162.2, 99.2, 96.3	109.7, 104.2, 85.9	795
9	160.0, 154.9, 152.6, 132.9, 100.5	105.6, 84.9, 65.4, −1.1	806
10	147.1, 143.2, 143.1, 141.2, 137.6, 122.0, 98.1	72.6, 36.8, 29.2, 14.1, 3.2	180
11	146.7, 144.0, 143.2, 141.2, 121.8, 115.7, 102.1	72.7, 36.4, 29.6, 23.9	187
13[b]	146.0, 144.7, 143.6, 140.9, 138.1, 132.6, 114.3	75.1, 26.3, 23.1, 17.7, 5.1	927
14[b]	145.6, 144.6, 143.6, 140.9, 132.5, 128.8, 118.4	75.3, 26.1, 23.2[c]	932

[a] ^1H: **2**: 4.13; **3**: 3.05; **4**: 6.69, **7** 4.19; **8**: 6.74. ^{14}N: **3**: 39; **4**: 237; **8**: 238; **9**: 237.

[b] In CH_2Cl_2/C_6D_6.

[c] Relative integral intensities of peaks are 2:4:2.

Table 2
XRD data for compounds.

Compound	**3**	**5**	**9**	**12** $3H_2O$	**14**
Formula	$C_{16}H_{12}F_8N_2Se_2$	$C_{10}F_8N_2Se_2$	C_5ClF_4NSe	$C_5H_6F_4NSeO_3Na$	$C_{11}ClF_8NOSe$
Molecular weight	542.20	458.04	264.47	306.05	428.53
Temperature, K	293	296	200	200	200
Syngony	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	P – 1 (No. 2)	P-1 (No. 2)
a (Å)	15.354(3)	5.2916(5)	23.9579(15)	6.1763(4)	10.8044(11)
b (Å)	7.9550(16)	17.8512(15)	7.2127(6)	7.5180(5)	14.3303(18)
c (Å)	17.029(3)	13.6042(15)	8.7725(8)	11.0469(8)	14.5808(18)
α (°)	90	90	90	107.125(2)	116.766(3)
β (°)	116.62(3)	93.834(7)	100.383(6)	95.469(2)	99.675(4)
γ (°)	90	90	90	96.683(2)	96.025(4)
V (Å^3)	1859.5(8)	1282.2(2)	1491.1(2)	482.32(6)	1944.7(4)
Z	4	4	8	2	6
$D_{calc.}$ (g/cm^3)	1.937	2.373	2.356	2.107	1.905
$F(000)$	1048	856	992	296	1074
μ (mm^{-1})	4.058	5.861	5.403	3.985	2.163
Crystal size (mm)	$0.40 \times 0.20 \times 0.10$	$0.90 \times 0.10 \times 0.06$	$0.40 \times 0.30 \times 0.20$	$0.50 \times 0.30 \times 0.04$	$0.55 \times 0.35 \times 0.20$
θ range(°)	2.4–27.5	1.9–28.0	2.6–28.0	2.0–32.5	1.6–27.1
Indices	$-19 \le h \le 0$, $0 \le k \le 10$, $-19 \le l \le 22$	$-6 \le h \le 0$, $-23 \le k \le 0$, $-17 \le l \le 17$	$-31 \le h \le 31$, $0 \le k \le 9$, $0 \le l \le 11$	$-8 \le h \le 9$, $-11 \le k \le 11$, $-16 \le l \le 16$	$-13 \le h \le 13$, $-18 \le k \le 18$, $-18 \le l \le 18$
Collected reflections	4365	3204	3840	16338	54431
Independent reflections	4209 ($R_{int} = 0.032$)	3085 ($R_{int} = 0.059$)	3600 ($R_{int} = 0.024$)	3250 ($R_{int} = 0.042$)	8531 ($R_{int} = 0.043$)
Reflections [$I > 2\sigma(I)$]	2589	2007	2774	3053	7053
Completeness to θ (%)	98.4	100.0	99.5	93.0	99.4
Abs. correction	Empirical	Integration	Empirical	Empirical	Empirical
Min./max. Transmitance	0.53/0.85	0.52/0.71	0.77/0.99	0.52/0.75	0.38/0.67
Data/restrains/parameters	4209/0/253	3085/0/199	3600/0/217	3250/6/136	8531/0/622
Goodness of fit on F^2	1.03	1.03	1.09	1.11	1.18
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0488$, $wR_2 = 0.1091$	$R_1 = 0.0441$, $wR_2 = 0.0896$	$R_1 = 0.0402$, $wR_2 = 0.0967$	$R_1 = 0.0199$, $wR_2 = 0.0474$	$R_1 = 0.0648$, $wR_2 = 0.2180$
R indices (all data)	$R_1 = 0.0896$, $wR_2 = 0.1306$	$R_1 = 0.0810$, $wR_2 = 0.1044$	$R_1 = 0.0594$, $wR_2 = 0.1059$	$R_1 = 0.0224$, $wR_2 = 0.0537$	$R_1 = 0.0779$, $wR_2 = 0.2292$

Table 3
Isolated yields, melting points, and MS and UV–vis data for compounds.[a,b]

Compound	Yield, %	M.p., °C	MS, *m/z*, found/calc.
1	51	100–102	521.7591/521.7596
2	57	73–74	517.8569/517.8570
3	77	79–81	543.9203/543.9203
4	68	106–108	423.8450/423.8453
5	24	88–90	459.8255/459.8264
6	95	Oil	–
7	92	Oil	–
8	90	45–47	–
9	92	28–30	–
10	42	29–30	394.9055/394.9060
11	85	66–67	410.8754/410.8765
13	39	144–146	435.888/435.889[c]
14	77	142–143	429.878/429.878[d]

[a] UV–vis, λ, nm (lg ε): **1**: 242 (4.06), 264 (4.10), 348 (3.12); **2**: 201 (4.31), 219 (4.13), 276 (4.06), 343 (3.21); **3**: 226 (4.25), 249 (4.21), 326 (4.19); **4**: 265 (4.03), 345 (2.94); **5**: 273 (4.12), 346 (2.78).

[b] MS: ^{78}Se for **1**, **10** and **11**, ^{80}Se for other compounds, except **6**–**9** for which mass spectra were not obtained due to their instability under experimental conditions.

[c] $[M+Na]^+$.

[d] $[M+H]^+$.

Table 4
Analytical data for compounds.

Compound	Found/calculated, %			
	C	H	N	F
1	24.99/24.64	–	4.53/4.79	25.55/25.98
2	32.38/32.58	1.12/1.17	–	29.46/29.45
3	35.57/35.44	2.30/2.23	5.16/5.17	29.12/28.03
4	28.39/28.46	0.67/0.48	6.63/6.64	27.16/27,01
5	25.89/26.22	–	6.18/6.12	33.01/33.18
6	24.34/24.19	–	–	25.63/25.51
7	28.46/28.65	1.29/1.03	–	25.74/25.89
8[a]	24.56/24.36	0.65/0.41	5.74/5.68	23.52/23.12
9	22.76/22.71	–	5.01/5.30	29.10/28.73
10[b]	33.64/33.36	–	3.77/3.54	43.58/43.17
11[a]	32.17/32.03	–	3.73/3.40	36.30/36.84
13	32.53/32.06	–	3.71/3.40	41.04/41.49
14	30.72/30.83	–	3.25/3.27	35.47/35.47

[a] Cl: **6** 23.32/23.80; **7** 11.87/12.08; **8**, 14.27/14.38; **11**, 8.59/8.59.

[b] Se: **7** 26.70/26.90; **10**, 20.10/19.94, **11** 19.40/19.14.

*4.3.3. Selenides **10**, **11** and selenolate **12***

At ambient temperature and under argon, 38 mg (1 mmol) of $NaBH_4$ was added in small portions to a stirred solution of 0.5 mmol of **15** in 10 ml of ethanol or to solution of the same amount of **1** in 10 ml of its 1:1 mixture with Et_2O. After additional 5 min., solution of 200 mg (1.2 mmol) of C_5F_5N in 1 ml of ethanol was added. (a) The solvent was distilled off, and the residue extracted with hexane. Extract was evaporated and the residue sublimed at 30 °C/1 mm. The product was crystallized from ethanol at −20 °C. Compound **10** was obtained as white powder. Very minor reaction residue insoluble in hexane was crystallized from wet acetone. Compound $\mathbf{12}\cdot 3H_2O$ was obtained in the form of colorless crystals suitable to XRD. (b) The solvent was distilled off, and the residue crystallized from hexane at −20 °C. Compound **11** was obtained as white powder.

*4.3.4. Selenoxides **13** and **14***

At ambient temperature, 110 mg (0.7 mmol) of $KMnO_4$ were added in small portions to a stirred solution of 0.2 mmol of **10** or **11** in 5 ml of glacial acetic acid. After additional 30 min, (a) the solvent was distilled off and the residue sublimed at 110 °C/1 mm. Compound **13** was obtained in the form of white powder. (b) The reaction mixture was passed through short silica column (eluent: ethylacetate), and saturated aqueous $NaHCO_3$ was added to eluate. The resulted mixture was extracted with ethylacetate. Organic layer was separated, dried with $MgSO_4$, filtered and evaporated. Compound **14** was obtained in the form of white powder. Single crystals of **14** suitable to XRD were prepared by slow evaporation of CH_2Cl_2 solution.

Acknowledgments

The authors are grateful to Prof. Dr. Yuri V. Gatilov for valuable discussion of the XRD structures, to Dr. Vladimir I. Rodionov, Mr. Alexander M. Maksimov and Mr. Pavel V. Nikulshin for their generous gifts of the starting materials, to Prof. Dr. Valentina P. Fadeeva for elemental analysis for Se, and to the Collective Chemical Service Center of Siberian Branch of the Russian Academy of Sciences for instrumental facilities. A. G. M. thanks the Russian Science Support Foundation for a 2010–2011 Postgraduate Scholarship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.08.002.

References

[1] (a) T. Wirth (Ed.), Organoselenium Chemistry. Synthesis and Reactions, Wiley-VCH, 2011;
(b) A.J. Mukherjee, S.S. Zade, H.B. Singh, R.B. Sinoj, Chemical Reviews 110 (2010) 4357–4416;
(c) D.M. Freudendahl, T. Wirth, in: J.D. Woollins, R.S. Laitinen (Eds.), Selenium and Tellurium Chemistry From Small Molecules to Biomolecules and Materials, Springer, 2011, pp. 41–56;
(d) F. Devillanova (Ed.), Handbook of Chalcogen Chemistry, Royal Society of Chemistry, 2006.

[2] (a) A.G. Makarov, I.Yu. Bagryanskaya, Yu.V. Gatilov, N.V. Kuratieva, A.Yu. Makarov, M.M. Shakirov, A.V. Alexeyev, K. Tersago, C. Van Alsenoy, F. Blockhuys, A.V. Zibarev, European Journal of Inorganic Chemistry (2010) 4801–4810;
(b) K. Tersago, I.Yu. Bagryanskaya, Yu.V. Gatilov, S.A. Gromilov, A.Yu. Makarov, M. Mandado, C. Van Alsenoy, A.V. Zibarev, F. Blockhuys, European Journal of Inorganic Chemistry (2007) 1958–1965;
(c) A.Yu. Makarov, E. Lork, R. Mews, A.V. Zibarev, Journal of Fluorine Chemistry 127 (2006) 437–442;
(d) K. Tersago, M. Mandado, C. Van Alsenoy, I.Yu. Bagryanskaya, M.K. Kovalev, A.Yu. Makarov, Yu.V. Gatilov, M.M. Shakirov, A.V. Zibarev, F. Blockhuys, Chemical European Journal 11 (2005) 4544–4551;
(e) A.Yu. Makarov, I.G. Irtegova, N.V. Vasilieva, I.Yu. Bagryanskaya, T. Borrmann, Yu.V. Gatilov, E. Lork, R. Mews, W.D. Stohrer, A.V. Zibarev, Inorganic Chemistry 44 (2005) 7194–7199.

[3] (a) T.M. Klapoetke, B. Krumm, P. Meyer, Zeitschrift für Naturforschung B 59 (2004) 547–553;
(b) T.M. Klapoetke, B. Krumm, K. Polborn, European Journal of Inorganic Chemistry (1999) 1359–1366.

[4] A.Yu. Makarov, K. Tersago, K. Nivesanond, F. Blockhuys, C. Van Alsenoy, M.K. Kovalev, I.Yu. Bagryanskaya, Yu.V. Gatilov, M.M. Shakirov, A.V. Zibarev, Inorganic Chemistry 45 (2006) 2221–2228.

[5] (a) T.J. Emge, M.D. Romanelli, B.F. Moore, J.G. Brennan, Inorganic Chemistry 49 (2010) 7304–7312;
(b) A.L. Fuller, F.R. Knight, A.M.Z. Slawin, J.D. Woollins, European Journal of Inorganic Chemistry (2010) 4034–4043.

[6] (a) P. Howes, M. Green, C. Johnston, A. Crossley, Journal of Materials Chemistry 18 (2008) 3474–3480;
(b) A.M.M. Abeykoon, M. Castro-Colin, E.V. Anokhina, M.N. Iliev, W. Donner, A.J. Jacobson, S.C. Moss, Physical Review B 77 (2008) 075333/1;
(c) G. Kedarnath, L.B. Kumbhare, V.K. Jain, A. Wadawale, G.K. Dey, C. Thinaharan, S. Naveen, M.A. Sridhar, J.S. Prasad, Bulletin of the Chemical Society of Japan 81 (2008) 489–494;
(d) A. Dass, R. Guo, J.B. Tracy, R. Balasubramanian, A.D. Douglas, R.W. Murray, Langmuir 24 (2008) 310–315;
(e) J.G. Brennan, T. Siegrist, P. Caroll, S. Stuczynski, L. Brus, M.L. Steigerwald, Journal of the American Chemical Society 111 (1989) 4141–4143;
(f) J.G. Brennan, T. Siegrist, S. Stuczynski, P. Carroll, P. Rynders, L.E. Brus, M.L. Steigerwald, Chemistry of Materials 2 (1990) 403–409.

[7] (a) O.P. Dimitriev, N.A. Ogurtsov, A.A. Pud, P.S. Smertenko, Yu.P. Piryatinski, Yu.V. Noskov, A.S. Kutsenko, G.S. Shapoval, Journal of Physical Chemistry C 112 (2008) 14745–14753;
(b) F. Aslam, D.M. Graham, D.J. Binks, P. Dawson, N. Pickett, P. O'Brien, C.C. Byeon, D.-K. Ko, J. Lee, Journal of Applied Physics 103 (2008) 093702–093707;
(c) A.V. Firth, Y. Tao, D. Wang, J. Ding, F. Bensebaa, Journal of Materials Chemistry 15 (2005) 4367–4372;

(d) G. Kedarnath, S. Dey, V.K. Jain, G.K. Dey, B. Varghese, Polyhedron 25 (2006) 2383–2391.
[8] (a) A. Eichhoefer, O. Hampe, M. Blom, European Journal of Inorganic Chemistry (2003) 1307–1314;
(b) V.N. Soloviev, A. Eichhoefer, D. Fenske, U. Banin, Journal of the American Chemical Society 123 (2001) 2354–2364;
(c) V.N. Soloviev, A. Eichhoefer, D. Fenske, U. Banin, Journal of the American Chemical Society 122 (2000) 2673–2674;
(d) M.W. DeGroot, C. Khadka, H. Roesner, J.F. Corrigan, Journal of Cluster Science 17 (2006) 97–110;
(e) A. Eichhoefer, European Journal of Inorganic Chemistry (2005) 1245–1253.
[9] (a) X. Huang, J. Li, Journal of the American Chemical Society 129 (2007) 3157–3162;
(b) X. Huang, H.R. Heulings, V. Le, J. Li, Chemistry of Materials 13 (2001) 3754–3759;
(c) X. Huang, J. Li, H. Fu, Journal of the American Chemical Society 122 (2000) 8789–8790;
(d) S.Y. Girgis, A.M. Salem, M.S. Selim, Journal of Physics B 19 (2007) 116213/1.
[10] P.L. Coe, A.J. Rees, Journal of Fluorine Chemistry 101 (2000) 45–60.
[11] (a) J.T. Ayers, S.R. Anderson, Synthetic Communications 29 (1999) 351–358;
(b) M. Sakakibara, K. Katsumata, Y. Wanatabe, T. Toru, Y. Ueno, Synthesis (1992) 377–379;
(c) L.E. Overman, J. Smoot, J.D. Overman, Synthesis (1974) 59–60.
[12] P.W. Codding, K.A. Kerr, Acta Crystallographica B 35 (1979) 1261–1263.
[13] T.M. Klapoetke, B. Krumm, P. Mayer, H. Piotrowski, O.P. Ruscitti, Zeitschrift fur Naturforschung B57 (2002) 145–150.
[14] V.E. Platonov, A.M. Maksimov, K.V. Dvornikova, P.V. Nikulshin, Russian Journal of Organic Chemistry 41 (2005) 1647–1653.
[15] R.D. Chambers, D.J. Spring, Tetrahedron 27 (1971) 669–680.
[16] J. Burdon, W.B. Hollyhead, J.C. Tatlow, Journal of the Chemical Society (1965) 6336–6342.
[17] R.D. Chambers, F.D. Drakesmith, W.K.R. Musgrave, Journal of the Chemical Society (1965) 5045–5048.
[18] R.D. Chambers, J. Hutchinson, W.K.R. Musgrave, Journal of the Chemical Society (1964) 3573–3576.
[19] G.M. Sheldrick, Acta Crystallographica A 64 (2008) 112–122.
[20] (a) A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Version 10M, Utrecht University, The Netherlands, 2003;
(b) A.L. Spek, Journal of Applied Crystallography 36 (2003) 7–13.
[21] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Stree, Journal of Applied Crystallography 39 (2006) 453–457.