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Supramolecular synthesis based on a combination of Se…N secondary bonding interactions with hydrogen and halogen bonds

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The crystal structures of cocrystals of 2,1,3-benzoselenadiazoles with hydrogen or halogen bond donors have demonstrated that the [Se-N]₂ cyclic supramolecular synthon based on Se...N secondary bonding interaction (SBI) is quite reliable. The [Se-N]₂ dimers were found in 9 out of the 12 studied cocrystals and in two polymorphic forms of 4,5,6,7-tetramethyl-2,1,3benzoselenadiazole. These studies show that the [Se-N]₂ dimer can be used as a secondary building block for the construction of larger supramolecular assemblies or frameworks. It can bind to the molecules containing hydrogen- or halogen-bond donors and in some cases form additional SBIs with the use of selenadiazole binding sites that are not involved in the formation of the dimers. Binary discrete complexes were formed with monofunctional hydrogen or halogen bond donors like pentafluorophenol, pentafluorobenzoic acid or pentafluoroiodobenzene whereas one or two dimensional aggregates were found in complexes with bifunctional donors like resorcinol, tetrafluororesorcinol, tetrafluorohydroquinone and 1,4-diiodotetrafluorobenzene. It has been demonstrated that carboxylic acids and ortho-fluorophenols bind to the [Se-N]₂ dimers via cyclic synthons based on a combination of the O-H···N and N-Se···X (X = F, O) interactions. In turn, the geometry of the $C-I \cdots N$ halogen bond does not allow for the formation of an analogous cyclic synthon in the cocrystals of selenadiazoles with orthoflouroiodobenzenes.



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KEYWORDS: crystal engineering, secondary bonding interactions, cocrystals, 2,1,3benzoselenadiazoles, crystal structure

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ABSTRACT: Examination of the solid state structures of 2,1,3-benzoselenadiazole complexes with hydrogen or halogen bond donors has demonstrated that the 2,1,3-benzoselenadiazole molecules preferably form centrosymmetric dimers with use of [Se–N]₂ supramolecular synthon whereas the two remaining nitrogen atoms not involved in the [Se–N]₂ supramolecular interactions can act as acceptors of hydrogen or halogen bonds. Cocrystallization of selenadiazoles with monofunctional hydrogen or halogen bond donors like pentafluorophenol,

 pentafluorobenzoic acid or pentafluoroiodobenzene results in formation of binary discrete complexes. One or two dimensional aggregates based on selenadiazole $[Se-N]_2$ dimers as building blocks were prepared using bifunctional hydrogen or halogen bond donors like resorcinol, tetrafluororesorcinol, tetrafluorohydroquinone and 1,4-diiodotetrafluorobenzene. During the complexation of selenadiazoles with hydroquinone, anilic acid or chloranilic acid a competition between Se····N and Se····O interactions resulted in breaking of the $[Se-N]_2$ synthon.

Introduction

Secondary bonding interactions (SBIs) are of primary importance for supramolecular chemistry.¹⁻² There is a close analogy between X–A…Y SBIs and hydrogen bonding: both systems are basically linear, where X–A is a covalent bond and A…Y is a weak interaction. When A = H this interaction is described as a hydrogen bond and for A \neq H as a secondary bond. In specific cases when A is halogen, chalcogen or pnictogen atom these secondary interactions are also called halogen, chalcogen or pnictogen bonds, respectively.³⁻⁹ The X–A…Y interaction is strengthened by the presence of an electronegative substituent on the electronacceptor atom A and it gains strength as one moves down to heavier elements in the appropriate column of the periodic table. According to so called σ -hole theory,¹⁰⁻¹² noncovalent X-A…Y interaction between covalently-bonded atom A of Group IV-VII and a negative site Y involves a region of positive electrostatic potential, labeled a σ -hole, on the extension of the covalent bonds to the Group IV – VII atom. The features and properties of halogen, chalcogen or pnictogen bonds treated as σ -hole bonds are explained in terms of electrostatics, polarization and dispersion.

Scheme 1



1,2,5-Chalcogenadiazoles exhibit a remarkable tendency toward self-association into dimers and polymers by four-membered [Se–N]₂ or [Te–N]₂ cyclic supramolecular synthons (Scheme 1) involving two highly directional SBIs.¹³⁻²⁰ The strength of SBIs formed by 1,2,5-chalcogenadiazoles increases on going from sulphur to tellurium and as revealed by a survey of the Cambridge Structural Database (CSD)²¹ telluradiazoles frequently form polymers by [Te–N]₂ synthons, selenadiazoles form dimers whereas thiadiazoles²² most often are not associated.

We turned our attention to 2,1,3-benzoselenadiazoles which have attracted much less attention than analogous telluradiazoles showing stronger SBIs. These compounds are easily accessible in reaction of *o*-phenylenediamines with selenium dioxide²⁴ and are much better soluble in common organic solvents than the tellurium derivatives. Structural studies of several compounds of this class have demonstrated that due to self-complementary Se…N interactions they crystallize in a dimeric form (Fig. 1a-b).^{22,25-27} Interestingly, the parent 2,1,3-benzoselenadiazole (**1**) shows different behavior and the SBIs lead to a catemer motif in the solid state (Fig. 1c).²⁸

σ-hole



Figure. 1 a) Electrostatic potential map for 1 showing two σ -holes at the extension of N-Se bonds; b) dimeric and c) catemeric motifs via Se…N secondary interactions.

Se

Se

However, the dimeric units of **1** have been found in its cationic form as well as in some metal complexes of this compound.²⁹⁻³⁵ The 2,1,3-benzoselenadiazole dimers that are potential ditopic ligands for metal coordination have been recently used for the preparation of coordination polymers.³²⁻³⁵ Thus, it seems reasonable to expect that such dimers could be also

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used as building blocks for the construction of extended supramolecular frameworks with use of two remaining sp² nitrogen atoms not involved in the formation of a [Se–N]₂ synthon.

These N atoms create two potential acceptor sites for hydrogen, halogen or chalcogen bonds. This however raises the problem of competition of intermolecular interactions that might result in a disruption of the dimer structure and poses difficulties in the design and construction of ordered supramolecular architectures with use of the title compounds. More detailed studies of the structural competition between Se…N interactions and hydrogen or halogen bonding could help to develop supramolecular strategies that may accommodate two or more different interactions in such a way that they could produce predictable supramolecular assemblies.

Last but not least, the polar 2,1,3-benzoselenadiazole molecules may be engaged in aromaticring stacking interactions that, in general, should be orthogonal to the dimer plane. The selfassociation of these heterocyclic molecules *via* aromatic interactions may compete with the interactions involving aromatic rings bearing hydrogen or halogen bond donors. This competition should be particularly important in the case of single hydrogen or halogen bond donors attached to a perfluoroaryl skeleton as the aryl-perfluoroaryl interactions are particularly strong.³⁶⁻³⁷

In this contribution we report examples of supramolecular arrays created by complexation of 2,1,3-benzoselenadiazole (1) and its tetramethyl derivative (2) with several strong hydrogen bond donors, which include: resorcinol (**res**), hydroquinone (**hqu**), anilic acid (**ani**), chloranilic acid (**cla**), pentafluorophenol (**pfp**), pentafluorobenzoic acid (**pfb**), tetrafluororesorcinol (**tfr**) and tetrafluorohydroquinone (**tfq**). For comparison we also prepared the complex of 2,1,3-benzothiadiazole (3) with **pfp**. In the next step we studied structures of the complexes of 1 and 2

with halogen bond donors including pentafluoroiodobenzene (**pfi**), 1,4-diiodotetrafluorobenzene (**dib**), and iodine (**I**₂) (see Scheme 2).





Experimental

2,1,3-Benzoselenadiazole (1) An aqueous solution of selenium dioxide (2.31 g, 21 mmol) was added to 1,2-diaminobenzene (2.25 g, 21 mmol) in ethanol (15 mL), refluxed for 10' and cooled.

The collected white precipitate was recrystallized from hexane obtaining 3.85 g of the product; m.p. 78–79 °C (lit.^{38,39} m.p. 76 °C).

4,5,6,7-Tetramethyl -2,1,3-benzoselenadiazole (2) was obtained in a similar manner to 1;

m.p. 159–160 °C. ¹H NMR (CDCl₃) δ 2.68 (s, 6H), 2.68 (s, 2H), 2.35 (s, 6H); ¹³C NMR (CDCl₃) δ 160.3, 137.2, 125.7, 16.9, 15.0; Anal. Calcd for C₁₀H₁₂N₂Se (239): C, 50.22; H, 5.06; N, 11.71. Found: C, 50.20; H, 4.99; N, 11.59.

2,1,3-Benzothiadiazole (3) To a solution of commercial *o*-phenylenediamine (1 g, 9.25 mmol) in dry pyridine (15 ml) was added thionyl chloride (9 ml). The mixture was refluxed for 5 h, and then solvent was distilled off at reduced pressure. Water was added to the black residue. The precipitate was filtered and washed with water. The crude product was chromatographed on silica gel (AcOEt/hexane, 1:1) to give **3** as a white solid; m.p. 42-44 °C (lit. 38,40 m.p. 44 °C).

Single crystals of the reported complexes were prepared by dissolving 2,1,3benzochalcogenadiazole and the second crystal component in 1:1 (**pfp**, **pfb**, **pfi**) or 2:1 (**res**, **tfr**, **hqu**, **tfq**, **ani**, **cla**, **dib**) molar ratio in appropriate solvent (see text) and slow evaporation of the solution.

X-ray Crystallography. X-Ray diffraction data for 2β , 1·dib, 1·tfq, 1·ani were collected with an Oxford Diffraction Xcalibur diffractometer and those for 2·pfb, 1·cla with an Oxford Diffraction Supernova diffractometer. Data for the remaining crystals were measured with a KM4CCD diffractometer. The crystals were mounted on a plastic loop with the use of a lowdensity perfluoropolyether oil. The diffraction data were processed with the CrysAlis software.⁴¹ The crystal structures were solved by direct methods with SHELXS97⁴² and refined by fullmatrix least-squares with SHELXL-2014/7⁴³ within Olex-2.⁴⁴ The structure of 1·I₂ was determined from a non-merohedrally twinned specimen. Drawings were prepared with Olex-2⁴⁴

and Mercury⁴⁵ software. Crystal data and details of data reduction and structure refinement are given in Table 1.

Table 1. Crystal data and refinement details.

	2α	2β	1∙pfp	3∙pfp	1∙pfb
CCDC no.	1423307	1423308	1423304	1423311	1423302
Empirical formula	$C_{10}H_{12}N_2Se$	$C_{10}H_{12}N_2Se$	$\begin{array}{c} C_6H_4N_2Se{\cdot}C_6H_1F\\ {}_5O\end{array}$	$\begin{array}{c} C_6H_4N_2S{\cdot}C_6H_1F_5\\ O\end{array}$	$\begin{array}{c} C_6H_4N_2Se{\cdot}C_7H_1F\\ {}_5O_2\end{array}$
Formula weight	239.18	239.18	367.14	320.24	395.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Temperature, K	130	130	130	130	130
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P2_{1}/c$	C2/m	$P2_{1}/n$	<i>P</i> -1	$P2_{1}/c$
Unit cell dimensions, Å,°	a = 14.204(2)	a = 17.2005(3)	a = 4.4075(5)	a = 6.7990(6)	a = 14.1550(9)
	b = 3.9431(9)	b = 7.0255(1)	b = 10.8261(8)	b = 7.1071(5)	b = 6.6180(5)
	c = 16.645(3)	c = 8.4958(2)	c = 25.5327(16)	c = 13.1740(9)	c = 15.2148(13)
				$\alpha = 97.585(6)$	
	$\beta = 95.688(14)$	β = 111.357(2)	$\beta = 93.622(8)$	$\beta = 91.605(6)$	$\beta = 109.822(7)$
				$\gamma=107.503(7)$	
Volume, Å ³	927.6(3)	956.15(3)	1215.89(18)	600.25(8)	1340.85(18)
Z	4	4	4	2	4
Calculated density, g/cm ³	1.713	1.662	2.006	1.772	1.957

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Absorption coefficient, mm ⁻¹	3.998	3.879	3.152	0.334	2.871
2Θ range for data collection, [°]	8.65 to 52.74	8.46 to 52.72	8.18 to 52.74	8.56 to 52.72	8.24 to 52.74
Reflections collected	4507	8454	6453	6958	7704
Independent reflections	1881	1055	2489	2442	2737
R _{int} , R _{sigma}	0.0755, 0.0504	0.0241, 0.0109	0.0306, 0.0365	0.0179, 0.0246	0.0171, 0.0212
Data / restraints / parameters	1881/0/122	1055/0/83	2489/0/194	2442/0/190	2737/0/210
Goodness-of-fit on F ²	1.068	1.156	1.120	1.062	1.057
Final R indices [I>2 σ (I)]	$R_1 = 0.0578$	$R_1 = 0.0197,$	$R_1 = 0.0448$	$R_1 = 0.0348$	$R_1 = 0.0243$
	$wR_2 = 0.1509$	$wR_2 = 0.0561$	$wR_2 = 0.1020$	$wR_2 = 0.0938$	$wR_2 = 0.0579$
R indices (all data)	$R_1 = 0.0628$	$R_1 = 0.0197$	$R_1 = 0.0554$	$R_1 = 0.0464$	$R_1 = 0.0301$
	$wR_2 = 0.1559$	wR ₂ =0. 0.0561	$wR_2 = 0.1053$	$wR_2 = 0.0979$	$wR_2 = 0.0603$
Largest diff. peak and hole, eA ⁻³	1.51, -1.70	0.38, -0.33	0.95, -0.63	0.39, -0.26	0.50, -0.47

Table 1. continued

	2∙pfb	1_2 ·res	1₂∙hqu	2₂•tfr	1₂•tfq
CCDC no.	1423309	1423305	1423300	1423310	1423306
Empirical formula	$C_{10}H_{12}N_2Se\cdot$	$(C_6H_4N_2Se)_2$	$(C_6H_4N_2Se)_2$.	$(C_{10}H_{12}N_2Se)_2$.	$(C_6H_4N_2Se)_2$.
	$C_7H_1F_5O_2$	$C_6H_6O_2$	$C_6H_6O_2$	$C_6H_2F_4O_2$	$C_6H_2F_4O_2$
Formula weight	451.25	476.25	476.25	660.43	548.22
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Temperature, K	130	130	130	130	130
Wavelength, Å	1.54178	0.71073	0.71073	0.71073	0.71073
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	$P2_{1}/c$
Unit cell dimensions, Å	a = 7.4964(3)	a = 7.5664(7)	a = 6.7101(10)	a = 8.1807(6)	a = 9.3870(3)
	b = 7.8250(3)	b = 11.1094(10)	b = 7.1434(8)	b = 10.7132(10)	b = 5.8129(2)
	c = 15.3014(6)	c = 11.3805(11)	c = 9.7805(11)	c = 14.6161(11)	c = 16.7089(5)
	$\alpha = 101.120(3)$	$\alpha = 104.881(8)$	$\alpha = 97.557(9)$	$\alpha = 96.887(7)$	
	$\beta=100.098(3)$	$\beta = 100.371(8)$	$\beta = 90.810(10)$	$\beta = 94.200(6)$	$\beta = 97.489(3)$
	$\gamma = 93.800(3)$	$\gamma = 105.600(8)$	$\gamma = 112.066(12)$	$\gamma = 98.227(7)$	
Volume, Å ³	862.41(6)	858.01(15)	429.66(10)	1253.31(18)	903.96(5)
Z	2	2	1	2	2
Calculated density, g/cm ³	1.738	1.843	1.841	1.750	2.014

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Absorption coefficient, mm ⁻¹	3.590	4.331	4.324	3.014	4.156
2Θ range for data collection/°	14.13 to 136.47	8.21 to 52.74	8.43 to 52.74	8.18 to 52.74	8.27 to 52.74
Reflections collected	7839	6490	3490	13652	9648
Independent reflections	3143	3487	1741	5103	1847
R _{int} , R _{sigma}	0.0217, 0.0216	0.0175, 0.0291	0.0169, 0.0228	0.0391, 0.0637	0.0211, 0.0172
Data / restraints / parameters	3143/1/248	3487/1/236	1741/1/122	5103/2/348	1847/1/136
Goodness-of-fit on F ²	1.034	1.017	1.064	0.970	1.070
Final R indices [I>2 σ (I)]	R ₁ =0.0334,	R ₁ =0.0245,	R ₁ =0.0206	R ₁ =0.0385	R ₁ =0.0179
	wR ₂ =0.0862	$wR_2 = 0.0586$	wR ₂ =0.0523	wR ₂ =0.0742	wR ₂ =0.0451
R indices (all data)	R ₁ =0.0346,	R ₁ =0.0316,	R ₁ =0.0226	R ₁ =0.0651	R ₁ =0.0206
	wR ₂ =0.0875	wR ₂ =0.0610	wR ₂ =0.0530	wR ₂ =0.0818	wR ₂ =0.0463
Largest diff. peak and hole, eA ⁻³	0.70, -0.82	0.62, -0.57	0.47, -0.62	0.77, -0.54	0.32, -0.32

Table 1. continued

	1 ₂ ·ani	1·cla	1∙pfi	1 ₂ ·dib	$1 \cdot I_2$
CCDC no.	1423297	1423298	1423303	1423299	1423301
Empirical formula	$(C_6H_4N_2Se)_2$	$C_6H_4N_2Se$	$C_6H_4N_2Se$	$(C_6H_4N_2Se)_2$	$C_6H_4N_2Se\cdot I_2$
	$C_6H_4O_4$	$C_6H_2Cl_2O_4$	C_6F_5I	$C_6F_4I_2$	
Formula weight	506.24	392.05	477.03	768.00	436.87
Crystal system	Monoclinic	Monoclinic	Monoclinic	monoclinic	Monoclinic
Temperature, K	298	298	130	293	293
Wavelength, Å	0.71073	1.54184	0.71073	0.71073	0.71073
Space group	$P2_{1}/n$	C2/c	$P2_{1}/n$	$P2_{1}/c$	$P2_{1}/c$
Unit cell dimensions, Å	a = 4.94419(19)	a = 17.6480(5)	a = 6.9525(5)	a = 19.4639(7)	a = 4.5056(7)
	b = 26.8020(13)	b = 8.7634(2)	b = 25.5310(13)	b = 10.8098(5)	b = 10.5200(17)
	c = 6.8526(3)	c = 9.4163(3)	c = 15.3220(9)	c = 15.5794(7)	c = 20.541(3)
	$\beta = 93.345(4)$	$\beta = 113.834(4)$	$\beta=100.243(5)$	$\beta = 101.574(4)$	$\beta = 94.649(13)$
Volume, Å ³	906.51(6)	1332.10(7)	2676.4(3)	3211.3(3)	970.4(3)
Z	2	4	8	6	4
Calculated density, g/cm ³	1.855	1.955	2.368	2.383	2.990

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Absorption coefficient, mm ⁻¹	4.113	7.695	5.164	6.386	10.173
2Θ range for data collection/°	8.40 to 52.74	13.87 to 148.99	8.26 to 52.734	8.33 to 50.05	8.71 to 50.05
Reflections collected	5696	7903	14997	29091	4377
Independent reflections	1847	1354	5441	5652	1611
R _{int} , R _{sigma}	0.0169, 0.0185	0.0259, 0.0141	0.0195, 0.0273	0.0597, 0.0512	0.0629, 0.0504
Data / restraints / parameters	1847/1/128	1354/1/96	5441/0/379	5652/0/407	1611/78/101
Goodness-of-fit on F ²	1.109	1.097	1.083	1.026	1.240
Final R indices [I>2 σ (I)]	R ₁ =0.0254,	R ₁ =0.0308,	R ₁ =0.0278	R ₁ =0.0394	R ₁ =0.0867
	wR ₂ =0.0595	wR ₂ =0.0835	wR ₂ =0.0590	wR ₂ =0.0669	wR ₂ =0.2689
R indices (all data)	R ₁ =0.0318,	R ₁ =0.0320,	R ₁ =0.0408	R ₁ =0.0624	R ₁ =0.0925
	wR ₂ =0.0619	wR ₂ =0.0850	wR ₂ =0.0627	wR ₂ =0.0743	wR ₂ =0.2824
Largest diff. peak and hole, eA ⁻³	0.30, -0.28	0.33, -0.76	0.85, -0.71	0.68, -0.54	4.12, -2.50

Results and discussion

2,1,3-Benzoselenadiazoles 1 and 2 were obtained by heating of the corresponding ophenylenediamines with selenium dioxide in ethanol.²³⁻²⁴ 2.1.3-Benzothiadiazole (3) was prepared by reaction of o-phenylenediamine with thionyl chloride in pyridine at room temperature.⁴⁶ Compound 2 was obtained in two polymorphic forms: needles 2α (m.p. 159-160 °C; $P2_1/c$, Z'=1) grown from ethanol and needles 2 β (m.p. 139-140 °C, C2/m, Z'=0.5) prepared by evaporation from toluene. In both cases the selenadiazole molecules form centrosymmetric dimers through the [Se–N]₂ supramolecular synthon with coplanarly oriented heterocyclic units. The Se···N distances of 2.905(3) and 2.911(2) Å in 2α and 2β , respectively, are *ca*. 0.2 Å shorter than those found in the catemer structure of 1 $(3.155 \text{ Å})^{28}$ and are close to the mean value of 2.90(5) Å calculated for ten 2,1,3-benzoselenadiazole dimers found in the CSD (ver. 5.36 plus three updates).²¹ The N-Se···N interactions in the two polymorphs are not linear (see Table 2) but deviations of the N-Se····N angle from 180° are similar to those found in the other dimers [the mean value 165(4)°]. The Se atom of 1,2,5-selenadiazole has a potential to form two SBIs directed to the extensions of two Se-N bonds, however in the polymorphs of 2, analogously to the crystal structure of 1, the chalcogen atom participates only in one short contact (Table 2). The main difference between the two crystalline forms of 2 is in the assembly mode through aromatic ring interactions. The dimeric units in 2α are arranged into translational stacks along the b axis (Fig. 2a) with the interplanar distance of 3.504 Å and the distance between the centroids of the benzene and 1,2,5-selenadiazole rings is of 3.753 Å. In contrast, the structure of 2β revealed that the dimers, which have all their non-H atoms located on a mirror plane, aggregate in a simple brick-wall motif parallel to (001) with the [Se-N]₂ synthons located in a row just over the gap between the dimers in the rows below and above (Fig. 2b). The closest distance between the

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centroids of the benzene rings within the brick-wall is 3.749 Å and the interplanar distance is 3.513 Å. According to the melting point values and the crystal densities, which are 1.713 g cm⁻³ for 2α and 1.661 g cm⁻³ for 2β at 130 K, the polymorph 2α is a more stable form than 2β .



Figure 2. The N-Se····N and aromatic-ring stacking interactions between the dimers of **2** in the polymorph 2α (a) and the polymorph 2β (b). The hydrogen atoms are omitted for clarity.

X- A ··· Y	X-A [Å]	A…Y [Å]	<x-a…y [°]<="" th=""><th>X…Y[Å]</th><th>Symmetry code</th></x-a…y>	X…Y[Å]	Symmetry code
2α					
$N3-Se2\cdots N1^{i}$	1.793(4)	2.905(4)	168.0(1)		1-x,2-y,-z
2β					
$N3-Se2\cdots N1^i$	1.795(2)	2.911(2)	165.76(8)		2-x, y, 1-z
l∙pfp					
N1-Se2…N3 ⁱ	1.801(4)	2.941(4)	164.3(1)		-x,1-y,1-z
N3-Se2…F6A	1.790(4)	3.247(3)	159.8(1)		
O1A-H1A…N1	0.80(5)	1.95(5)	160(5)	2.709(5)	

3.pfp

N3-S2…F6A	1.606(2)	3.064(1)	168.78(6)		
O1A-H1A…N1	0.84	2.00	154	2.777(2)	
l∙pfb					
N1-Se2…N3 ⁱ	1.791(2)	2.851(2)	162.45(6)		2-x,1-y,1-z
N3-Se2…O2A	1.783(2)	3.127(2)	163.18(6)		
O1A-H1A…N1	0.84	1.81	173	2.641(2)	
2∙pfb					
N1-Se2…N3 ⁱ	1.797(2)	3.021(2)	163.40(8)		1-x, 2-y, 1-z
N3-Se2…O2A	1.786(2)	3.073(2)	167.47(8)		
O1A-H1A…N1	0.84	1.82	179	2.656(3)	
1_2 ·res					
N31-Se21N12	1.787(2)	2.925(2)	172.48(8)		
N32-Se22…N11	1.783(2)	3.262(2)	163.14(8)		
$N12$ -Se22 \cdots O1 A^{i}	1.777(2)	3.178(2)	166.12(7)		1-x, 1-y, 2-z
N11-Se21····C4A ⁱ	1.789(2)	3.376(2)	164.83(8)		-1+x, y, -1+z
01A-H1A…N32	0.84	2.13	2.940(3)	163	
$O2A-H2A\cdots N31^{i}$	0.84	1.98	2.809(3)	170	1-x,1-y,1-z
1 ₂ ·hqu					
N1-Se2…O1A ⁱ	1.790(2)	3.142(2)	163.91(6)		x-1, y, z
N3-Se2…O1A ⁱ	1.778(2)	3.278(2)	158.00(6)		1-x,-y,1-z
$O1A-H1A\cdots N1^i$	0.84	1.98	172	2.815(2)	x+1,y,z
$C7-H7\cdots N3^{i}$	0.95	2.51	163	3.431(2)	x+1,y,z

2 ₂ •tfr					
$N11$ -Se 21 ····N 31^{i}	1.799(3)	2.874(3)	167.3(1)		2-x, 1-y, 1-z
$N12$ -Se 22 ···· $N32^{i}$	1.795(4)	2.903(4)	169.1(1)		-1-x, -y, 1-z
N31-Se21····F2A	1.791(4)	3.048(2)	169.1(1)		
N32-Se22····F4A	1.788(4)	2.837(2)	173.2(1)		
O3A-H3A…N12	0.84	2.01	153	2.781(5)	
O1A-H1A…N11	0.84	1.98	161	2.790(5)	
1₂∙tfq					
$N3-Se2\cdots N1^i$	1.793(1)	2.891(1)	165.60(5)		-x,-y,1-z
N1-Se2…F3A ⁱ	1.792(1)	3.122(1)	161.67(5)		1-x,2-y,1-z
O1A-H1A…N3	0.84	1.90	165	2.718(2)	
1 ₂ ·ani					
$N1$ -Se2 \cdots O1 A^{i}	1.782(2)	3.254(2)	173.06(7)		x,y,1+z
N3-Se2…O3A ⁱ	1.779(2)	2.851(2)	169.26(8)		2-x,1-y,1-z
O1A-H1A…N1	0.84	1.95	168	2.781(2)	
С7-Н7…N3	0.93	2.54	166	3.453(3)	x,y,-1+z
$C8-H8\cdotsO1^{i}$	0.93	2.63	165	3.533(3)	2-x, 1-y, -z
1·cla					
N1-Se2····O3A ⁱ	1.773(2)	3.399(2)	158.26(7)		0.5+x,0.5-y, -0.5+z
O1A-H1A…N1	0.84	1.93	153	2.708(2)	
C4-H4····Cl2A	0.93	2.76	152	3.607(2)	
1∙pfi					
N12-Se22N31	1.796(3)	2.972(3)	164.4 (1)		

1.786(3)	3.070(3)	163.1 (1)	
2.085(4)	3.073(3)	171.2 (1)	
2.077(3)	2.961(3)	174.8 (1)	
1.787(3)	3.289(3)	171.4(1)	0.5+x, 0.5-y, 0.5+z
1.787(3)	3.308(3)	133.6(1)	1.5-x, -0.5-y,0.5-z
1.790(5)	2.905 (5)	168.2 (2)	
1.786 (5)	3.025 (4)	164.5 (2)	
1.796 (4)	2.922 (5)	167.4 (2)	-x, 1-y, 1-z
2.084 (5)	3.001 (5)	175.8 (2)	
2.092 (5)	3.016 (5)	176.7 (2)	
2.066 (5)	3.104 (4)	175.2 (2)	1+x, 0.5-y, 0.5+z
1.804 (2)	2.804 (2)	164.5 (6)	1-x, 2-y, -z
2.734 (2)	2.636 (2)	172.1 (4)	
2.734 (2)	3.756 (2)	137.7 (6)	-x, -0.5+y,- 0.5-z
	1.786(3) 2.085(4) 2.077(3) 1.787(3) 1.787(3) 1.787(3) 1.790(5) 1.786 (5) 1.796 (4) 2.084 (5) 2.092 (5) 2.066 (5) 1.804 (2) 2.734 (2) 2.734 (2)	 1.786(3) 3.070(3) 2.085(4) 3.073(3) 2.077(3) 2.961(3) 1.787(3) 3.289(3) 1.787(3) 3.308(3) 1.787(3) 3.308(3) 1.790(5) 2.905 (5) 1.786 (5) 3.025 (4) 1.796 (4) 2.922 (5) 2.084 (5) 3.001 (5) 2.092 (5) 3.016 (5) 2.066 (5) 3.104 (4) 1.804 (2) 2.804 (2) 2.734 (2) 3.756 (2) 	1.786(3) $3.070(3)$ $163.1(1)$ $2.085(4)$ $3.073(3)$ $171.2(1)$ $2.077(3)$ $2.961(3)$ $174.8(1)$ $1.787(3)$ $3.289(3)$ $171.4(1)$ $1.787(3)$ $3.289(3)$ $171.4(1)$ $1.787(3)$ $3.308(3)$ $133.6(1)$ $1.790(5)$ $2.905(5)$ $168.2(2)$ $1.786(5)$ $3.025(4)$ $164.5(2)$ $1.796(4)$ $2.922(5)$ $167.4(2)$ $2.084(5)$ $3.001(5)$ $175.8(2)$ $2.092(5)$ $3.016(5)$ $176.7(2)$ $2.066(5)$ $3.104(4)$ $175.2(2)$ $1.804(2)$ $2.804(2)$ $164.5(6)$ $2.734(2)$ $2.636(2)$ $172.1(4)$ $2.734(2)$ $3.756(2)$ $137.7(6)$





Figure 3. Tetrameric assemblies in **1**•**pfp** organized into translational stacks along the *a* axis. The C-bound H atoms are omitted for clarity.



Figure 4. Stacks of heterodimers in **3**•**pfp.** The distances between the centroid of the benzene ring of **pfp** and the centroids of the 1,2,5-thiadiazole and benzene rings of **3** are 3.484-3.625 Å and 3.583-3.652 Å, respectively. The C-bound H atoms are omitted for clarity.

Diffraction quality crystals of the molecular complexes of **1** and **3** with **pfp** were grown from hexane. The crystal structure of the 1:1 complex **1**•**pfp** (P2₁/*n*, Z'=1; m.p. 83-84°C) showed that the molecules of **1** form the [Se–N]₂ dimers that bind two molecules of **pfp** through O–H···N hydrogen bonds, creating centrosymmetric nearly planar four-component assemblies (Fig. 3, Table 2). Interestingly, the Se atom forms another short contact to a fluorine substituent of the

Se2…F6A distance of 3.247(3) Å is *ca*. 0.1 Å shorter than the sum of the van der Waals radii of F and Se $(3.47 \text{ Å})^{47}$ and the N-Se···F angle is 159.8(1)°. This interaction orients the **pfp** molecule essentially in one plane with 1. The heterotetramers are further organized into slipped stacks along the *a* axis in such a way that the aryl-perfluoroaryl interactions are excluded. Instead, the 2,1,3-benzoselenadiazole dimers are arranged into separate translational stacks, very similar to those in the polymorph 2α , with the centroid-centroid distance between the benzene and 1,2,5-selenadiazole rings of 3.755 Å and the interplanar distance of 3.455 Å. The aromatic rings of **pfp** molecules arranged into stacks along the b axis do not overlap but their F2A and F5A atoms are placed directly above and below the centroids of the adjacent benzene rings, with the centroid...F distances being of 3.209 and 3.201 Å, respectively. In contrast, the 1:1 **3** pfp adduct ($P\overline{1}$, Z'=1; m.p. 59-60°C) is composed of virtually planar heterodimers formed via O-H…N hydrogen bond, accompanied again by N-S…F interaction (S…F distance 3.064 Å), without any indication of the S…N SBI. This is in line with our expectations because S…N interaction is weaker than Se...N SBI and 2,1,3-benzothiadiazoles do not form $[S-N]_2$ dimers. The heterodimers are further assembled into stacks along the *a* axis with the alternating arrangement of the 2,1,3-benzothiadiazole and perfluorophenol molecules (Fig. 4).



Figure 5. Heterotetramers formed *via* N-Se…N, N-Se…O and O-H…N interactions in **1**•**pfb** and **2**•**pfb** (left) and their packing in the crystals (right). The C-H hydrogen atoms are omitted for clarity.

Analogously to **1**•**pfp**, the crystals of the 1:1 complexes **1**•**pfb** (crystallization from CH₂Cl₂, m.p. 84-85°C; $P2_1/n$, Z'=1) and **2**•**pfb** (crystallization from n-hexane/CH₂Cl₂, m.p. 142-145°C; $P\overline{1}$, Z'=1) are composed of the four-component aggregates involving the selenadiazole dimers associated with two molecules of **pfb** through O–H···N hydrogen bonds and Se···O interaction (Fig. 5). Pentafluorobenzoic acid, with the pKa value of 1.48,⁴⁸ belongs to strong organic acids,

however no proton transfer from the carboxylic group to the imine N atoms of 1 or 2 had occurred. In both complexes the Se atoms are involved in two SBIs and the carboxylic acid molecule binds to selenadiozole unit through the cyclic six-membered synthon involving O– H…N and N–Se…O interactions. The geometry of the Se…X (X=N,O) contacts slightly differs in the two structures (Table 2): in 1•pfb the Se…N contact is 0.28 Å shorter than the Se…O one whereas in 2•pfb these two distances are similar (3.021 and 3.073 Å, respectively). Interestingly, even though the two complexes differ in space group symmetry, $P_{21/C}$ versus $P \bar{1}$, their supramolecular organization is quite similar as illustrated in Fig. 5. In both structures, the selenadiazole dimers are arranged into a brick-wall via π - π stacking interactions. In 1•pfb the centroid-centroid distance between the benzene and 1,2,5-selenadiazole rings is 3.589 Å and the mean interplanar distance between the molecules of 1, that are inclined by 3.0°, is 3.273 Å. In 2•pfb distances between the analogous ring centroids are 3.601 and 3.920 Å and the interplanar distances between strictly parallel molecules of 2 are 3.448 and 3.521 Å.





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Figure 6. (a) Hexa-component aggregate *via* N–Se····N, O–H··· N and π - π stacking interactions in **1**₂·**res** and (b) the (010) layer formed from these aggregates *via* N–Se····O and N–Se··· π interactions. The C- H hydrogen atoms are omitted for clarity.

Since the above results confirmed our expectations concerning interaction modes of hydrogen bond donors with selenadiazoles we tried in the next step to construct higher dimensional aggregates using bifunctional hydrogen bond donors such as resorcinol (**res**) or hydroquinone (**hqu**). Additionally, to explore the reliability of the cyclic synthon observed in **1**•**pfp** involving the O–H…N and N–Se…F interactions, perfluoroanalogues of **res** and **hqu**, 2,4,5,6tetrafluororesorcine (**tfr**) and 2,3,5,6-tetrafluorohydroquinone (**tfq**), were also included in this study.

The colorless plates of the 2:1 complex $1_2 \cdot res$ (m.p. 62-63°C; $P\overline{1}$, Z'=1) were obtained by a slow evaporation from methanol. Its crystal structure revealed a centrosymmetric hexacomponent aggregate composed of two stacked dimers of **1** held together by four O–H··· N hydrogen bonds (Fig. 6a). In this arrangement, two planar dimeric units of **1** are positioned by the hydroxyl groups of **res** such that they lie stacked alongside of each resorcinol unit. This kind of structure closely resembles those of the resorcinol cocrystals with bispyridyl derivatives reported by MacGilivray and coworkers.⁴⁹⁻⁵⁰ All N atoms of **1** are either hydrogen bonded by the phenolic groups or involved in the formation of dimers *via* [Se–N]₂ synthon, therefore a second SBI to Se atoms can only involve O atoms of the hydroxy groups or π -electrons of the aromatic rings. In the case of Se22, a short contact is formed to the oxygen atom of **res** with the Se22… O1A distance being ca. 0.1 Å shorter than the Se22… N11 contact in the dimer (Table 2). In turn the Se21 atom of the second symmetry independent molecule of **1** interacts additionally with π -electrons of the aromatic ring of **res**. These interactions organize the hexameric aggregates into (010) layer shown in Fig. 6b.



Figure 7. Crystal structure of 1_2 ·hqu: (a) the (001) layer-type substructure generated via O– H…N hydrogen bonds and N-Se…O interactions; (b) the (10-1) layer-type substructure generated *via* N-Se…O interactions and aromatic ring interactions; (c) 3D crystal packing with marked (001) and (10-1) substructures. The C- H hydrogen atoms are omitted for clarity.

Cocrystallization of **1** with hydroquinone (**hqu**) afforded 2:1 **1**₂•**hqu** complex ($P\overline{1}$, Z'=0.5; plates from CH₂Cl₂-methanol, m.p. 106-107°C) that in contrast with **1**₂•**res** does not contain selenadiazole dimers. This structure, with **hqu** molecule located around inversion center, is determined not only by the expected O–H····N hydrogen bonds connecting **hqu** with two molecules of **1** but also by rather weak N-Se···O SBIs of the Se atom with two hydroxy oxygen atoms (Table 2). A cooperation between the O–H···N and N–Se···O interactions results in a layered structure parallel to (001) shown in Fig 7a. There are two cyclic motifs within this

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structure: the eight-membered ring involving two O–H···N hydrogen bonds and two Se···O (3.278 Å) contacts, and the four-membered ring involving two different Se···O interactions (3.277 and 3.142 Å). In turn, a cooperation between Se···O interactions, stacking interactions between the molecules of **1** and C-H··· π interactions between the edges of **1** and faces of **hqu** molecules results in another layer-type substructure parallel to (10-1) shown in Fig 7b. A combination of these two 2D substructures leads to a characteristic 3D crystal packing (Fig. 7c) that was previously described for 2:1 complexes of **hqu** with phenazine⁵¹ and quinoxaline.⁵²





Figure 8. Crystal structure of 2_2 •tfr: (a) 1D supramolecular polymer created from [Se–N]₂ dimers of 2 bridged by interactions with tfr; (b) aromatic-ring stacking interactions (c) crystal packing viewed along the *a* axis.

In the 2:1 complex 2_2 ·tfr ($P\bar{1}$, Z'=1; prisms from CH₂Cl₂-n-hexane, m.p. 162-163°C) the crystal structure is constructed from 1D supramolecular polymer created from [Se–N]₂ dimers of **2** bridged by interactions with tetrafluororesorcinol (tfr). The presence of the electonegative fluorine substituents at *ortho* positions to the hydroxy groups results in the formation of two cyclic synthons based on a combination of the N–Se…F and O-H…N interactions, analogously to those observed in **1**·pfp. In contrast with res and hqu complexes, where this cyclic synthon could not be formed, the interacting components show a nearly coplanar arrangement and form infinite ribbons running along the [310] direction (Table 2, Fig. 8a,c). The parallel oriented ribbons are stacked into (010) layers by π - π interactions between the benzene rings of **2** and tfr (the ring centroids distances 3.561 and 3.680 Å) and benzene rings of **2** (the ring centroids distances 3.784 Å) (Fig. 8b).



Figure 9. Crystal structure of 1_2 ·tfq: (a) 1D supramolecular polymer created from [Se–N]₂ dimers of 1 bridged by interactions with tfq; (b) aromatic-ring interactions (c) crystal packing viewed along the *b* axis.

(c)

(b)

Essentially planar 1D polymers generated by the same set of supramolecular synthons as in **2₂·tfr** are also found in the structure of the 2:1 complex **1₂·tfq** ($P2_1/c$, Z'=0.5; yellow prisms from CH₂Cl₂-heptane with a drop of MeOH, m.p. 150–151 °C; see Table 2 and Fig. 9a). Owing

to a different shape of the polymer, only local stacks composed of a 1_2 ·tfq triad are created *via* π - π interactions between the benzene ring of tfq and selenadiazole rings of 1 (the centroidcentroid distance 3.575 Å; Fig. 9b). This triad is connected with two other triads by the C-H··· π interactions between the benzene fragments of 1 (H···ring centroid distance 2.77 Å).



Figure 10. Crystal structure of 1_2 ·ani: (a) centrosymmetric heterotrimers *via* O–H····N hydrogen bond and N-Se···O interaction connected into wide supramolecular ribbons by weaker N–Se···O, C-H···N and C-H···O interactions; (b) crystal packing of the ribbons viewed along the *a* axis.







Anilic (ani) and chloranilic (cla; $pK_a = 0.73$) acids are benzoquinone-type molecules that undergo multi-stage deprotonation and protonation processes. In effect they are able to form with nitrogen heterocycles three types of hydrogen bonds: $O-H\cdots N$, $N^+-H\cdots O$ and $N^+-H\cdots O^-$. A combination of the last two creates bifurcated interactions (Scheme 3) useful in crystal engineering.⁵³⁻⁵⁴ On the other hand, the presence of the carbonyl oxygen *ortho* to the hydroxyl group at the benzene ring can promote the formation of competitive interactions leading to a seven-membered cyclic synthon via the O-H···N and C=O···Se interactions, similar to a cyclic synthon created in the cocrystals of selenadiazoles with *ortho*-fluorophenols (Scheme 3). To explore this competition we prepared a 2:1 complexes 1_2 and $(P2_1/n, Z'=0.5)$; brown needles, m.p. 159–160°C) and a 1:1 complex 1·cla (C2/c, Z'=0.5; red prisms, m.p. 231–232°C with dec.) by cocrystallization of the components from MeOH. The molecular components in both cocrystals are neutral and no [Se-N]2 dimers are created. Instead, their crystal structures are dominated by a cyclic seven-membered synthon involving O-H···N hydrogen bond and N-Se...O SBI (Table 2). In 1_2 and this synthon results in the formation of centrosymmetric heterotrimers containing one unit of **ani** that binds two molecules of **1**. They are further

assembled by the weaker N-Se···O, C-H···N and C-H···O interactions into wide planar ribbons extended along the *c* axis (Fig. 10). In the cocrystal **1·cla**, where **cla** is located around an inversion center and **1** at a twofold symmetry axis, the seven-membered cyclic synthon organizes the molecules into infinite [101] tapes, however the C=O···Se interaction is much weaker here than that in **1**₂**·ani**, with the O···Se distance of 3.399 Å approaching the sum of the van der Waals radii of O and Se (3.42 Å). These chains closely pack into (001) sheets with the formation of the short C–H···Cl contacts (Fig. 11). In both cocrystals there are no significant π - π stacking interactions between the aromatic rings with all distances between ring centroids exceeding 4.0 Å.



Figure 11. The (001) sheets in **1**·**cla** created through C–H···Cl interactions between [101] ribbons of molecules connected *via* O–H···N hydrogen bonds and weak C=O···Se interactions.

Halogen bonding, being an important example of SBI, has recently played an increasingly prominent role as design element in the crystal engineering and molecular recognition.^{3-6,55-57} There are numerous examples of supramolecular systems based on a combination of hydrogen and halogen bonds,⁵⁸⁻⁶⁶ however, the systems involving halogen bonds in combination with other SBI are to the best of our knowledge unknown. Thus the cocrystallization of 2,1,3-

benzoselenadiazoles with several halogen bond donors should shed some light on effectiveness of such a combination in the synthesis of supramolecular architectures. Particularly, a question of a structural competition between the Se…N, I…N and a possible Se…I interaction should be addressed.⁶⁷



Figure 12. Heterotetramers *via* N–Se····N and C–I····N interactions in **1·pfi** (left) and their packing into a 3D network through stacking interactions between **pfi** and **1** (right). Distances between the centroids of the benzene rings within the stack along [100] are 3.475 - 3.704 Å.



Figure 13. Crystal structure of 1_2 ·dib: (a) two symmetry independent chains *via* N–Se····N and C–I···N interactions; (b) two symmetry independent stacks *via* aromatic ring interactions between 1 and dib; (c) crystal packing viewed down the *b* axis. The H atoms are omitted for clarity.

Cocrystallization of **1** with pentafluoroiodobenzene (**pfi**) from hexane afforded colorless plates (m.p. 59-60 °C) of the 1:1 complex **1·pfi** ($P2_1/n$, Z'=2). The crystals contain heterotetramers composed of the [Se–N]₂ dimers formed by two symmetry independent molecules of **1** halogen bonded to two symmetry independent molecules of **pfi** (Table 2, Fig. 12). These tetramers are organized into a 3D network due to the aryl–perfluoroaryl interactions (Fig. 12). The molecular components are alternating along two symmetry independent stacks propagating along the *a* axis. The structure of **1·pfi** resembles that of **1·pfp** as both structures are composed of

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heterotetramers, however the geometry of $C-I\cdots N$ interaction hinders the formation a cyclic synthon involving $F\cdots$ Se contact that was present in **1**·**pfp**. Instead, the Se atoms interact weakly with F atoms of the symmetry related tetramers.

A complexation of **1** with 1,4-diiodotetrafluorobenzene (**dib**) leads to the 2:1 complex 1_2 ·**dib** (crystallization from CHCl₃, m.p. 89-91°C; P2₁/c, Z'=1.5) with a chain structure, where the [Se-N]₂ dimers of **1** are connected by halogen bonds to the **dib** molecules forming two symmetry independent chains (Table 2, Fig. 13a). The chains are further organized into a 3D structure by stacking interactions between the aromatic molecules (Fig. 13b,c). Two symmetry independent stacks along the *b* axis are created by pairs of **1** alternating with **dib** molecules. The distance between the centroids of **1** is of 3.640-3.772 Å, whereas that between the benzene-ring centroids of **1** and **dib** is of 3.682 – 4.039 Å.



Figure 14. 2D structure in $1 \cdot I_2$ created *via* N–Se····N, C–I···N and I–I···Se interactions. H atoms are omitted for clarity.

Cocrystallization of **1** with iodine results in a 1:1 complex $1 \cdot I_2$ (crystallization from CH₂Cl₂, m.p. 71-73°C; P2₁/c, Z'=1) consisting of 2D layers formed by interactions of the I_2 molecules

with the [Se–N]₂ dimers of **1**. The halogen molecule is involved in the I–I···N halogen bond where it plays a role of the electron acceptor and the N–Se···I chalcogen bond where it acts as the electron donor. The I···N and Se···I contacts are of 2.637 and 3.756 Å, respectively, and are shorter than the sums of the corresponding van der Waals radii of 3.53 and 3.88 Å, respectively.⁴⁷ The I···N value is within the range observed for the iodine complexes with nitrogen heterocycles⁶⁸ pointing to a relatively strong interaction. It also leads to a slight elongation of the I–I bond (2.734 Å) relative to the value in elemental iodine in its crystalline phase (2.718 Å)⁶⁹ due to a donation of the electron density to the antibonding n– σ * orbital of iodine. In contrast, the Se···I contact is only slightly shorter than the sum of the corresponding van der Waals radii and the I–I···Se angle of 137.7°, instead of being within 90–120°,⁷⁰⁻⁷¹ points to a weak interaction.

Concluding remarks

In this study we have demonstrated that the $[Se-N]_2$ cyclic supramolecular synthon based on Se…N secondary bonding interactions is quite reliable. The $[Se-N]_2$ dimers were found in 9 out of the 12 studied cocrystals of 2,1,3-benzoselenadiazoles and in two polymorphic forms of the 4,5,6,7-tetramethyl-2,1,3-benzoselenadiazole. Moreover, it has been shown that the $[Se-N]_2$ dimer can be used as a secondary building block for the construction of larger supramolecular assemblies or frameworks. It can bind to the molecules containing hydrogen- or halogen-bond donors and in some cases form additional SBIs with the use of selenadiazole binding sites not involved in the formation of the dimers. Carboxylic acids and *ortho*-fluorophenols bind to the $[Se-N]_2$ dimers *via* cyclic synthons based on a combination of the O–H…N and N–Se…X (X = F, O) interactions. In turn, the geometry of C–I…N halogen bond does not allow for the

formation of an analogous cyclic synthon in the cocrystals of selenadiazoles with *ortho*-flouroiodobenzenes.

In the cocrystals with anilic and chloranilic acids where the $[Se-N]_2$ dimers have been absent, the O-H···N and N-Se···O interactions resulting in the formation of a cyclic heterosynthon compete successfully with S···N SBI.

Supporting Information Available:

Ortep drawings with atom labeling system and crystallographic information files (CIF), are included in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supramolecular synthesis based on a combination of Se…N secondary bonding interactions with hydrogen and halogen bonds

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The 1,2,5-selenadiazole $[Se-N]_2$ dimer can be used as a secodary building block for the construction of supramolecular frameworks with hydrogen and halogen bonds.