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Organic selenocyanates as strong and directional chalcogen bond donors for crystal engineering†

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Organic bis(selenocyanate) derivatives act as powerful chalcogen bond donors for the elaboration of 1D extended structures upon co-crystallization with 4,4′-bipyridine as a ditopic chalcogen bond acceptor.

The renaissance of halogen bonding[1] in the last 20 years is largely rooted in the development of crystal engineering strategies[2] for the controlled formation of extended polymeric 1D, 2D or 3D structures through co-crystal formation.[3] For example, the association of *para*-diiodotetrafluorobenzene as a ditopic halogen bond donor with a large variety of Lewis bases[4] has led today to more than 220 structurally characterized co-crystals.[5] The efficiency of halogen bonding finds here its origin in its predictability, a direct consequence of its directionality due to the highly localized σ-hole which develops on the halogen atom.[6] This concept of σ-hole is not restricted to halogens but is also found in the heaviest elements of groups 14–16.[7] In the chalcogen series, calculations performed on molecules like $S(CN)_2$, $Se(CN)_2$,[8] and $Cl_3C–S–CN$,[9] show indeed the presence of two sizeable σ-hole sites on the chalcogen atoms, in the prolongation of the two C–S(Se) bonds, also confirmed by an experimental charge density determination on selenophtalic anhydride.[10] Nevertheless, the specific use of chalcogen bond donors in crystal engineering for the elaboration of extended 1D, 2D or 3D solid state structures is up to now very limited, probably because the presence of the two σ-holes limits the required predictability of the interaction. One can mention however self-assembly through chalcogen bonding in molecules like benzo-2,1,3-selenadiazoles,[11] benzo-1,3-tellurazoles,[12] or iso-tellurazole N-oxides,[13] bearing simultaneously an activated chalcogen atom and a Lewis base. Also, the close proximity of two chalcogen atoms in activated bithiophene or biselenophene derivatives can be used to chelate small anions through chalcogen bonding.[14] There are however no examples of the formation of chalcogen-bonded co-crystals associating for example a ditopic chalcogen bond donor with a ditopic Lewis base as a chalcogen bond acceptor, in a vein similar to the very successful examples introduced in halogen-bonded systems with α,ω-diiodoperfluoroalkanes[15] or *para*-diiodotetrafluorobenzene.[4]

In that respect, we considered organic selenocyanates R–Se–CN as potentially efficient chalcogen bond donors. It is expected indeed that the electron-withdrawing nature of the nitrile group will favour the formation of one single strong σ-hole on the selenium atom, in the prolongation of the NC–Se bond. A CSD investigation of reported structures of organic selenocyanates confirmed our initial assumption.[16] Indeed, most of the simple aliphatic and aromatic organic selenocyanates do crystallise with chalcogen bond interactions. In the absence of other Lewis bases, the selenium atom actually interacts with the nitrogen atom of a neighbouring selenocyanate moiety, giving rise to recurrent chain-like motifs, as in benzylselenocyanate (Fig. 1a),[17] and *ortho*-bis(selenocyanatomethyl)benzene,[18] (Fig. 1b) or *para*-bis(selenocyanatomethyl)benzene.[19]

Note the Se···N distances are in the range of 2.97–3.11 Å, *i.e.* notably shorter than 3.45 Å, the sum of the van der Waals radii

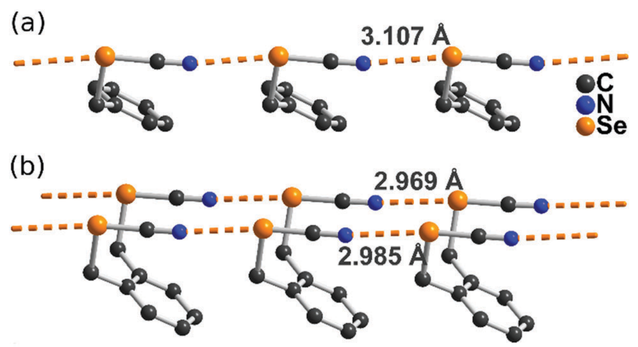

Fig. 1 Detail of the reported solid state structures of (a) benzylselenocyanate and (b) *ortho*-bis(selenocyanatomethyl)benzene. H atoms have been omitted and the orange dotted lines indicate the chalcogen bond interaction.

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† CCDC 1557620–1557622, Cif files for the X-ray crystal structures of **2**, (**2**·bipy) and (**3**·bipy). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc04833e

of Se (1.90 Å) and nitrogen (1.55 Å). The recurrence of this robust Se···N chalcogen-bonded motif lets us infer that specifically the three ditopic *ortho*-, *meta*- and *para*-bis(selenocyanatomethyl)benzenes, noted **1–3** in the following, could be themselves very good candidates to prepare, by analogy with diiodo derivatives mentioned above, co-crystals exhibiting similar predictable 1D supramolecular motifs. We therefore investigated the co-crystallisation of these three ditopic chalcogen bond donors **1–3** with, as a first example of a ditopic Lewis base, 4,4′-bipyridine, as detailed below.

The preparation of the three chalcogen bond donors **1–3** is based on the reaction of potassium selenocyanate with the *ortho*-, *meta*- and *para*-bis(bromomethyl)benzene in acetone, as described earlier.[19,20] The solid state structure of the *meta* isomer **2** was unknown, at variance with those of the *ortho* and *para* isomers **1** and **3**.[18,19] Compound **2** crystallises in the monoclinic system, space group *Cc*, with two crystallographically independent molecules in the unit cell (Fig. 2).‡

The molecules are again associated through short Se···N chalcogen bonds forming chains running along the *a* direction. Structural characteristics of these chalcogen bonds (Table 1) were compared with those reported earlier for the *ortho* and *para* derivatives (Fig. 1b and c), showing the same strong linearity, with a notable reduction ratio,[21] between 0.86 and 0.88. Note also that the robustness of this supramolecular Se···N motif most probably finds a further origin in the cooperativity it can develop along the chains. Indeed, the formation of the chalcogen bond on the nitrogen side leads to a decreased charge density on this atom, and by extension on the covalently linked selenium atom, whose electrophilic character is then enhanced. Such cooperativity effects have been demonstrated from theoretical calculations[22,23] on dimer, trimer and infinite one-dimensional chain models formed by $Se(CN)_2$ or $Te(CN)_2$, as these compounds adopt indeed this 1D motif in their experimental solid state structures.[24,25]

The formation of co-crystals between **1–3** and 4,4′-bipyridine was performed *via* diffusion of Et_2O over an acetone solution of both partners in equimolar quantities. Despite our efforts, good quality crystals were obtained only from **2** and **3**, affording 1 : 1 adducts. (**2**·bipy) crystallises in the monoclinic system, space group *C*2/*c*, with the *meta* derivative **2** located on a two-fold axis, and the 4,4′-bipyridine on an inversion centre, hence the 1 : 1 stoichiometry. As shown in Fig. 3, the nitrogen atom of the pyridine moiety competes now efficiently with the nitrogen atom of the nitrile to engage in a short and directional chalcogen bond, whose structural characteristics are collected in Table 2. This gives rise to the formation of hetero-molecular chains running along the (**4a–c**) direction. Note the particularly strong chalcogen bonding interaction, with a reduction ratio[21] down to 0.82 and a strong linearity, while the orientation of the lone pair of the pyridine moiety is not fully optimal since the angle between the $N_{bipy}–C_\gamma$ molecular axis and the Se···N direction amounts to only 165°.

Table 1 Chalcogen bond characteristics of the crystalline **1–3** derivatives

	Se···N (Å)	C–Se···N (°)	Se···N≡C (°)	Ref.
2				
Se1	3.010(24)	172.9(7)	172(2)	This work
Se2	3.015(24)	174.1(7)	173(2)	
Se3	2.965(24)	175.9(7)	174(2)	
Se4	3.017(24)	175.7(7)	176(2)	
3				
Se1	3.022(18)	171.8(5)	166(1)	19
Se2	2.997(18)	174.4(8)	177(2)	
1				
Se1	2.969(9)	172.6(3)	174.0(7)	18
Se2	2.985(8)	172.9(3)	173.2(7)	

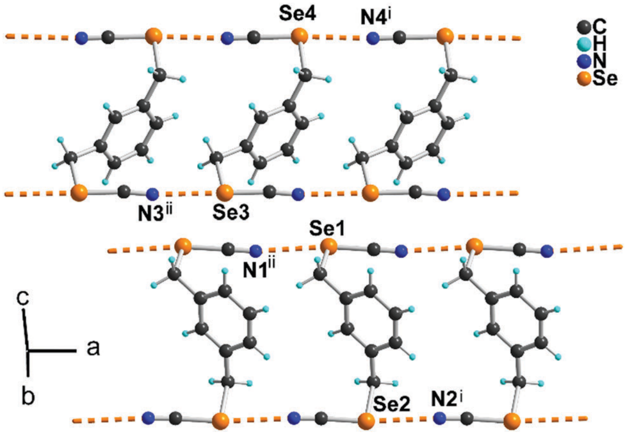

Fig. 2 Solid state organization of **2**, showing the chains formed out of the two crystallographically independent molecules. Symmetry operations: (i) 1 + x, y, z; (ii) −1 + x, y, z. The orange dotted lines indicate the chalcogen bond interaction.

The efficiency of this chalcogen-bonding motif is also evidenced from the crystal structure obtained with the *para* isomer, namely (**3**·bipy). It crystallises in the triclinic system, space group $P\bar{1}$, with both *meta*-bis(selenocyanatomethyl)benzene **3** and 4,4′-bipyridine located on inversion centres, hence the 1 : 1 stoichiometry. As shown in Fig. 4, chalcogen bonding interactions between the ditopic donors and acceptors again favour the formation of chains, running here along the (**2a–c**) direction, with structural characteristics (Table 2) comparable to those found in (**2**·bipy).

In conclusion, we have highlighted here the very strong tendency of organic selenocyanates to self-crystallise through efficient Se···N≡C chalcogen bonding interactions. Competitive crystallizations of bis-selenocyanates with a stronger ditopic Lewis base (4,4′-bipyridine) leads to recurrent 1D structures with directional and even shorter $Se···N_{bipy}$ chalcogen bonds. These examples

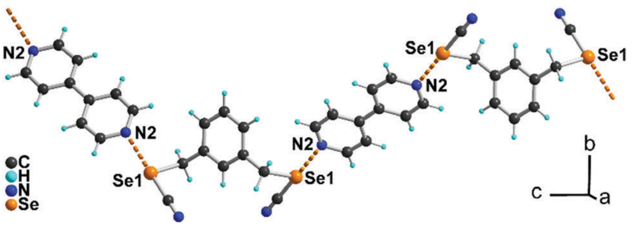

Fig. 3 Detail of one chalcogen-bonded chain running along the (4 + x, y, −1 + z) direction in (**2**·bipy). The orange dotted lines indicate the chalcogen bond interaction.

Table 2 Chalcogen bond characteristics of the (**2**·bipy) and (**3**·bipy) co-crystals

	Se···N (Å)	C–Se···N (°)	Se···N–C$_\gamma$ (°)
(**2**·bipy)	2.830(3)	177.2(1)	165.0(1)
(**3**·bipy)	2.897(4)	176.7(1)	165.9(1)

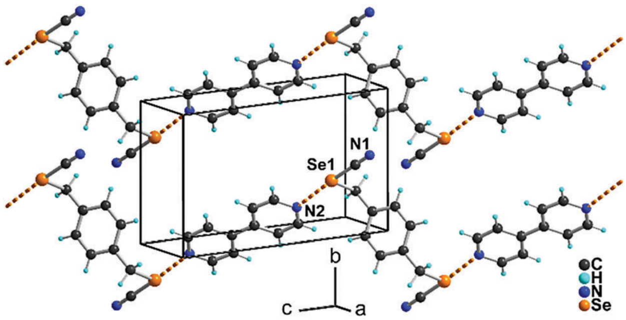

Fig. 4 Detail of one chalcogen-bonded chain running along the (**2a–c**) direction in (**3**·bipy). The orange dotted lines indicate the chalcogen bond interaction.

demonstrate that organic selenocyanates are efficient building blocks in crystal engineering strategies. By analogy with halogen bonding, they can probably be used also for other applications, such as liquid crystals and gels, anion recognition or organocatalysis.

Notes and references

‡ Crystal data for **2**: $C_{10}H_8N_2Se_2$, M = 314.10 g mol^{-1}, crystal dimensions 0.21 × 0.02 × 0.01 mm, monoclinic, space group Cc, a = 5.9696(7) Å, b = 36.720(4) Å, c = 10.2124(11) Å, β = 95.401(6)°, V = 2228.7(4) Å^3, Z = 8, ρ_{calcd} = 1.872 g cm^{-3}, F(000) = 1200, μ = 6.597 mm^{-1}, T = 293 K, $2\theta_{\max}$ = 55.37°. Final results (for 253 parameters) were R_1 = 0.0529, wR_2 = 0.10 and S = 1.018 for 3849 independent reflections [2328 with $I > 2\sigma(I)$]. Crystal data for (**2**·bipy): $C_{20}H_{16}N_4Se_2$, M = 470.29 g mol^{-1}, crystal dimensions 0.13 × 0.08 × 0.04 mm, monoclinic, space group $C2/c$, a = 5.1880(5) Å, b = 14.9962(13) Å, c = 25.101(2) Å, β = 92.613(3)°, V = 1950.8(3) Å^3, Z = 4, ρ_{calcd} = 1.601 g cm^{-3}, F(000) = 928, μ = 3.801 mm^{-1}, T = 293 K, $2\theta_{\max}$ = 61.158°. Final results (for 119 parameters) were R_1 = 0.037, wR_2 = 0.0877 and S = 1.03 for 3010 independent reflections [2147 with $I > 2\sigma(I)$]. Crystal data for (**3**·bipy): $C_{20}H_{16}N_4Se_2$, M = 470.29 g mol^{-1}, crystal dimensions 0.36 × 0.34 × 0.06 mm, triclinic, space group $P\bar{1}$, a = 5.3962(4) Å, b = 7.7356(6) Å, c = 11.7477(9) Å, α = 99.421(3), β = 94.558(2), γ = 104.661(2)°, V = 464.25(6) Å^3, Z = 1, ρ_{calcd} = 1.682 g cm^{-3}, F(000) = 232, μ = 3.993 mm^{-1}, T = 293 K, $2\theta_{\max}$ = 61.102°. Final results (for 118 parameters) were R_1 = 0.0412, wR_2 = 0.0841 and S = 1.022 for 2831 reflections [2161 with $I > 2\sigma(I)$].

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