

Supramolecular Synthesis Based on a Combination of Se⋯N Secondary Bonding Interactions with Hydrogen and Halogen Bonds

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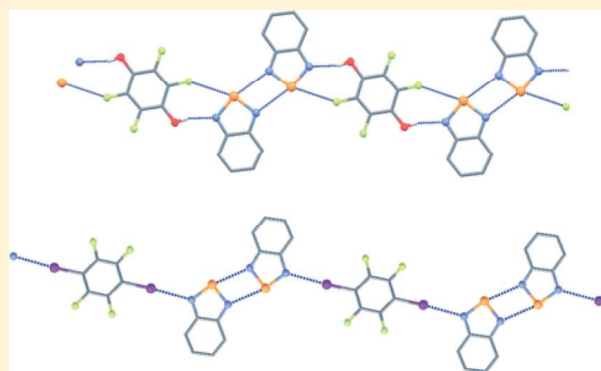
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Supporting Information

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.

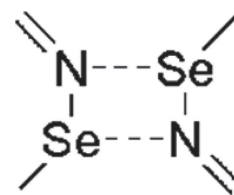


INTRODUCTION

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 ≠ 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 electron-acceptor 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.

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

Scheme 1



SBIs.^{13–20} The strength of SBIs formed by 1,2,5-chalcogenadiazoles increases on going from sulfur 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 more 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

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