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Short Note

Cocrystal of 4-Nitrophenol and 2,1,3-Benzoselenadizole

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Abstract: The 1:1 cocrystal of 4-nitrophenol (NP) and 2,1,3-benzoselenadiazole (BSA) was successfully synthesized. The X-ray single-crystal diffraction analysis revealed that the structure contained a $[Se–N]_2$ cyclic supramolecular synthon. The synthons were connected into a one-dimensional ribbon by O–H···N hydrogen bonds and N–Se···O chalcogen bonds. Furthermore, adjacent ribbons were stabilized by the π···π stacking interactions between two 2,1,3-benzoselenadiazole molecules, leading to the formation of a two-dimensional network.

Keywords: cocrystal; X-ray crystallography; non-covalent interaction

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1. Introduction

In recent years, organic cocrystals of variable stoichiometry based on intermolecular interactions became an active area in crystal engineering [1–3]. Non-covalent interactions between the cocrystal-building units play very important roles for the formation of molecular aggregates [4–6]. Among these interactions, the hydrogen bond is the most important and appears in most crystal structures [7]. Simultaneously, a π···π stacking interaction, halogen bond, and chalcogen bond are also extensively studied in supramolecular assembling [8]. The synthon approach was successfully used in the construction of supramolecular cocrystals. The aromatic heterocyclic compound 2,1,3-benzoselenadiazole (BSA) has received considerable attention for its ability to form a dimeric homosynthon based on a pair of Se···N chalcogen bonds, showing a short Se···N distance (2.80~3.26 Å) in a series of cocrystal compounds [9]. Meanwhile, The supramolecular heterosynthon including 2,1,3-benzoselenadiazole was also found in crystal engineering as a useful synthetic tool [10,11]. In this context, 2,1,3-benzoselenadiazole is often used as building block in a variety of supramolecular architectures; here, 2,1,3-benzoselenadiazole was used in the reaction with 4-nitrophenol (NP), and a new supramolecular cocrystal compound (**1**) was assembled and structurally characterized.

2. Results

The synthesized supramolecular compound was crystallized in a monoclinic $P2_1/c$ space group, having an equimolar ratio (1:1) of 2,1,3-benzoselenadiazole and 4-nitrophenol in the asymmetric unit (Figure 1). In **1**, two BSA molecules are held together by a pair of Se···N chalcogen bonds [d(Se···N) 2.88 Å], generating the $[Se–N]_2$ cyclic supramolecular synthon. Each synthon is bonded to four NP molecules via two intermolecular O–H···N hydrogen bonds [d(H···N) 1.96 Å] and two N–Se···O chalcogen bonds [d(Se···O) 3.37 Å]. With these interactions, adjacent BSA and NP molecules are linked together into an infinite one-dimensional chain, in which BSA synthons and NP molecules appear alternately. Furthermore, the chains are stabilized by the head-to-head π···π stacking interactions between the BSA molecules in two chains, forming a two-dimensional supramolecular network, as shown in Figure 2.

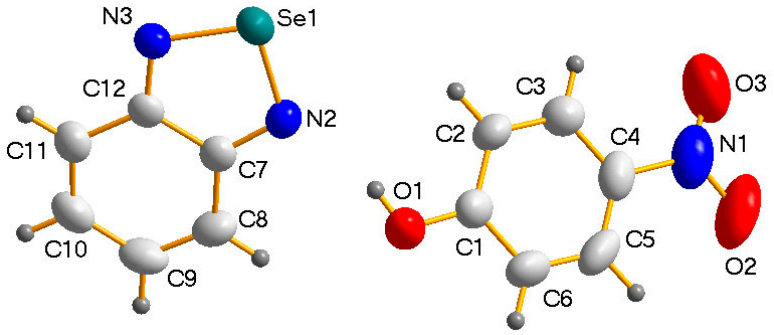

Figure 1. The molecular structure of **1** showing atom labeling and displacement ellipsoids at the 50% probability.

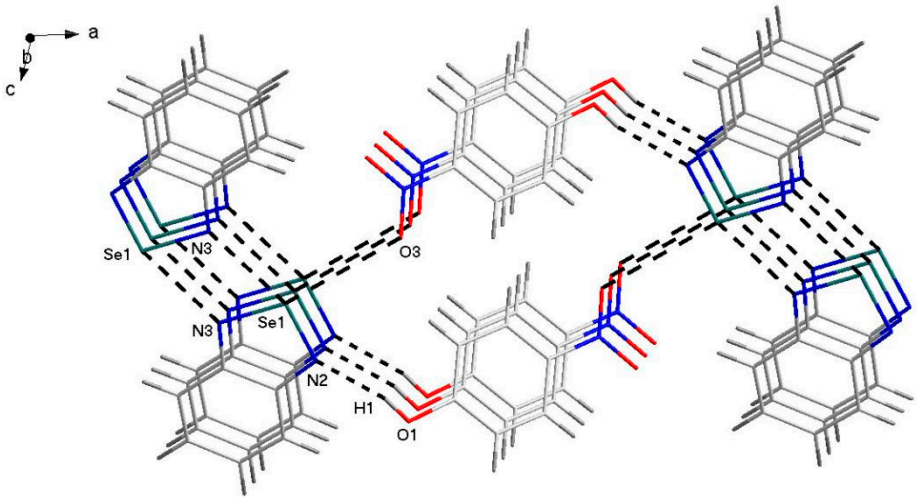

Figure 2. The 2D structure of **1**.

3. Materials and Methods

3.1. General Information

All chemicals and solvents were purchased from commercial sources and used without purification. The X-ray diffraction data were collected at 291 K on an Oxford Diffraction Gemini (Rigaku Corporation, Oxford, United Kingdom) with graphite-monochromated Mokα radiation (λ = 0.71073 Å). The Olex2 program was used as an interface, together with the SHELXT and SHELXL programs to solve the structure [12,13].

3.2. Synthesis and Characterization of **1**

A mixture of 2,1,3-benzoselenadiazole (0.183 g, 1 mmol) and 4-nitrophenol (0.139 g, 1 mmol) in 30 mL methanol was refluxed for 2 h. The resulting solution was allowed to slowly evaporate under ambient conditions. After a week, the product was collected as colorless crystals. Yield: 0.181 g, 56%.

Crystal data for C11H10N4S (**1**): M = 322.18, monoclinic, $P2_1/c$, a = 14.1004(10), b = 3.9390(2), c = 23.4020(15) Å, V = 1250.73(14) $Å^3$, Z = 4, D_x = 1.711 g cm^{-3}, *F*(000) = 640, and μ = 3.009 mm^{-1}. CCDC deposition number: 2250661.

The Supplementary Materials containing check CIF report, ^1H, ^{13}C NMR and XRD spectra of the title compound.

4. Conclusions

Thus, a new supramolecular cocrystal of 2,1,3-benzoselenadiazole and 4-nitrophenol was synthesized and characterized by single-crystal X-ray diffraction. The $[Se–N]_2$ homosynthon was also present in the cocrystal. The synthons were connected by O–H···N hydrogen bonds and N–Se···O chalcogen bonds into a one-dimensional chain, and the

two-dimensional network was formed by π···π stacking interactions between chains. The result shows that the synthon approach is helpful in the construction of supramolecular cocrystals.

Supplementary Materials: The following supporting information can be downloaded. Crystallographic data for (**1**) in crystallographic information file (CIF) format. CCDC 2250661 also contains the supplementary crystallographic data for this paper.

Author Contributions: W.W. conceived and designed the experiments; H.L. performed the experiments; S.M. and W.W. analyzed the data; H.L. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The authors confirm that the data supporting the findings of this study are available in the article and its Supplementary Materials.

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Conflicts of Interest: The author declares no conflict of interest.

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