

# Self-Assembly of Organo-Sulfur, Selenium and Tellurium Compounds via $\pi$ - $\pi$ -Stacking and Hydrogen Bonding Interactions

Berthold Kersting

Institut für Anorganische und Analytische Chemie, Universität Freiburg,  
Albertstr. 21, D-79104 Freiburg, Germany

Reprint requests to Dr. B. Kersting. E-mail: berthold.kersting@ac.uni-freiburg.de

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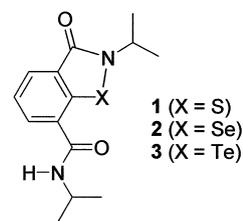
The crystal structures of 2-isopropyl-benzisothiazol-3-one-7-carboxylic acid isopropyl amide and of the corresponding selenium and tellurium derivatives have been determined. In contrast to the sulfur and selenium compounds, the tellurium derivative has an unprecedented three-dimensional network structure held together *via*  $\pi$ - $\pi$  stacking and hydrogen bonding interactions. The cavities in the 3D molecular network are filled with guest water molecules that are hydrogen bonded to carbonyl oxygen atoms.

## Introduction

The development of zeolite-like hybrid inorganic-organic or organic materials by self-assembly of complementary units is a mature but still growing research field [1]. The components of such materials are generally held together by directional forces that form extended frameworks of noncovalent interactions such as hydrogen bonds,  $\pi$ - $\pi$  interactions, or coordinative bonds [2]. Whereas the vast majority of low-density open organic frameworks represent one- or two-dimensional networks [3, 4], a major challenge is to control the assembly and solid-state structure in three dimensions [5]. We report herein on the self-assembly of the benzisotellurazole **3** which in the solid state is shown to exhibit an extended structure featuring a three-dimensional network. The crystal structures of the sulfur (**1**) and selenium analogs (**2**) are also presented.

## Results and Discussion

The benziisochalcogenazole derivatives **1** - **3** (see Scheme 1) are formally derived from isophthaloyl diamides [6, 7], which have a range of possible recognition sites: two amide groups for hydrogen bonding and an aromatic ring for  $\pi$ - $\pi$  stacking [8]. Incorporation of heteroatoms into the five-membered isochalcogenazole ring results in an alteration of the recognition sites in that one potential amide NH proton is no longer available for H-bonding.



Scheme 1. Structure of compounds **1** - **3**.

In addition, the variation of the heteroatom can influence the electronic structure of the heterocycles and this in turn can affect the strength of the  $\pi$ - $\pi$  stacking interactions [9]. To establish any structural differences, we determined the solid state structures of compounds **1** - **3** by single crystal X-ray analysis.

The crystal structure of **1** reveals the presence of discrete molecules (Fig. 1). There are two crystallographically independent molecules in the asymmetric unit. Since the two structures are essentially identical, the description will focus on molecule A. Table 1 lists selected bond lengths and angles. The benzisothiazole ring is nearly planar. The exocyclic amide group prefers a configuration with the carbonyl oxygen atom *trans* to the S-N bond, presumably for steric reasons. The C-S and S-N bond lengths are normal.

The individual molecules assemble *via* intermolecular N-H...O hydrogen bonding to yield cyclic tetrameric units (Fig. 2). Each molecule utilises its ring carbonyl oxygen atom and exocyclic

Table 1. Selected bond lengths [Å] and angles [°] in **1** - **3**.

	<b>1</b> (X = S) <sup>a</sup>	<b>2</b> (X = Se) <sup>a</sup>	<b>3</b> (X = Te)
C(1)-X(1)	1.728(3)	1.872(4)	2.051(4)
	[1.724(3)]	[1.864(4)]	
N(1)-X(1)	1.733(3)	1.906(3)	2.120(3)
	[1.726(3)]	[1.898(4)]	
O(2)···X(1)	2.484(3)	2.495(4)	2.463(3)
	[2.484(3)]	[2.453(4)]	
C(1)-X(1)-N(1)	89.4(1)	84.5(2)	78.3(1)
	[89.4(1)]	[84.7(2)]	

<sup>a</sup> There are two crystallographically independent molecules in the unit cell. Values in square brackets refer to the corresponding values of the second molecule.

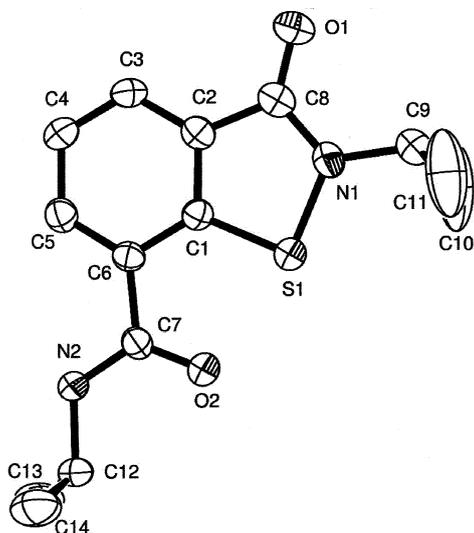


Fig. 1. Displacement ellipsoid plot of **1**. Hydrogen atoms are omitted for clarity.

amide NH proton, the corresponding O···N distances being 2.923 Å [N(4')-H···O(1)] and 2.977 Å [N(2)-H···O(3'')], respectively. The oxygen atom O(2) does not participate in hydrogen bonding. Note that there are no  $\pi$ - $\pi$  stacking interactions between the benzisothiazole rings.

The benzoselenazole **2** is isostructural with **1**. The molecular structure is depicted in Fig. 3. The Se-C and Se-N bond lengths are at 1.868(4) and 1.902(4) Å and compare well with those in other benzoselenazoles [10]. Similar to **1**, the selenium analog **2** forms two N-H···O hydrogen bonding interactions with two adjacent molecules (N-H···O

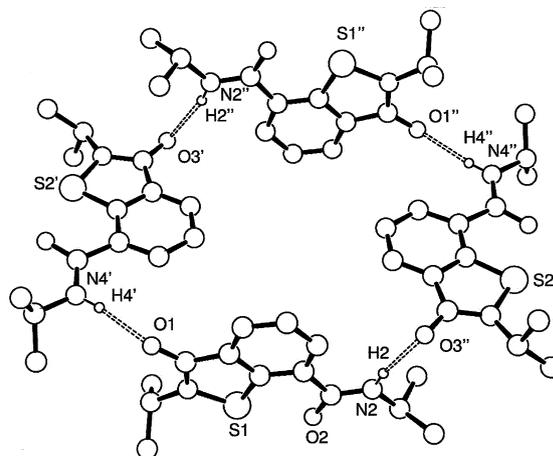


Fig. 2. Intermolecular hydrogen bonding interactions in **1** with atomic numbering scheme. Symmetry codes used to generate equivalent atoms:  $1-x, 0.5+y, 0.5-z$  (') and  $2-x, -y, -z$  (').

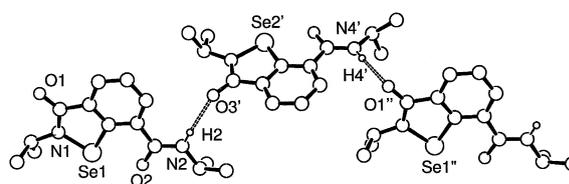


Fig. 3. Intermolecular hydrogen bonding interactions in **2** with atomic numbering for key atoms. Symmetry codes used to generate equivalent atoms:  $-x, 2-x, 1-z$  (') and  $-1+x, y, 1+z$  (').

at 2.858 and 2.918 Å), but in contrast to **1**, the molecules are linked in a one-dimensional fashion (see Fig. 3). Again, the structure shows no  $\pi$ - $\pi$  interactions.

The benzoselenazole **3**·H<sub>2</sub>O crystallises from ethyl acetate as beautiful pale-yellow crystals with a rhombic dodecahedral morphology. The space group determination indicated the space group  $Ia\bar{3}d$  (No. 230). On the molecular level, the structure of this compound is unexceptional: **3** is isostructural with **1** and **2** and the Te-C and Te-N bond lengths at 2.051(4) and 2.120(3) Å are similar to those of related organo-tellurium compounds [11]. Nevertheless, there are several features of the crystal structure which are worth considering: i) a three-dimensional network of neutral molecules held together by means of intermolecular  $\pi$ - $\pi$  stacking and hydrogen bonding interactions, ii) the inclusion of water molecules and iii) a system of non-interpenetrating small pore channels.

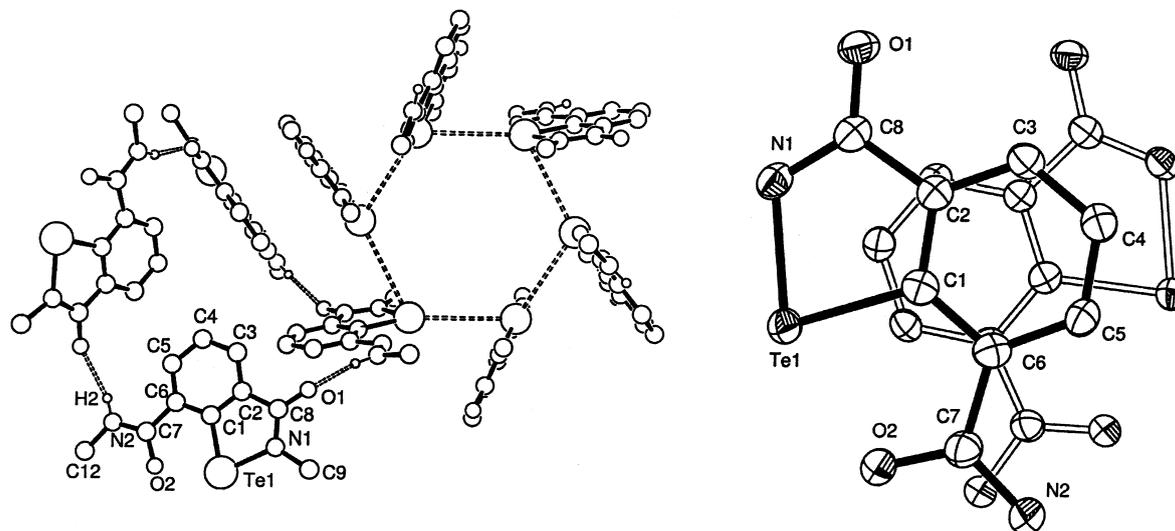


Fig. 4. Section of the three-dimensional network in  $3 \cdot \text{H}_2\text{O}$ . Isopropyl methyl carbon atoms and hydrogen atoms have been omitted for clarity. The view is along the  $[111]$  direction (left);  $\pi$ -stacking of the arene rings in  $3 \cdot \text{H}_2\text{O}$  (right).

The network of hydrogen bonds in  $3 \cdot \text{H}_2\text{O}$  is reminiscent of that of **1**, with four molecules linked *via* four  $\text{N-H} \cdots \text{O}$  hydrogen bonds ( $\text{N-H} \cdots \text{O}$ , 2.964 Å) to generate a cyclic tetramer (Fig. 4, left). The planar benzisotellurazoles of adjoining tetramers are further connected *via*  $\pi$ - $\pi$  stacking interactions. The stacking of the heterocycles is offset by *ca.* 0.4 Å and the average distance of any atom in the aryl ring to the mean plane of the adjacent ring is 3.45 Å (Fig. 4, right), which is approximately the optimal  $\pi$ -stacking distance [12].

The three-dimensional packing can alternatively be described by considering symmetry operations of the unit cell [13]. As can be seen in Fig. 4, six molecules are related by a crystallographic three-fold inversion axis at the midpoint of a  $\text{Te}_6$  hexagon. The six tellurium atoms are arranged in a chair-like conformation (torsion angle =  $33.6^\circ$ ) with a  $\text{Te} \cdots \text{Te}$  distance of 4.064(2) Å, thereby producing a hexagonal pore with a cross-section of *ca.* 4 Å. The observed  $\text{Te} \cdots \text{Te}$  distance is shorter than the sum of the van der Waals radii (4.20 Å), indicative of weak  $\text{Te} \cdots \text{Te}$  interactions [14]. These hexameric units stack along the  $\bar{3}$  axis, one rotated  $60^\circ$  relative to the other, with interlocking amide isopropyl residues (Fig. 5). As a consequence, porous channels are created along this direction (the viewing direction of Fig. 5). In this alternative description, the intermolecular  $\pi$ - $\pi$  stacking and hydro-

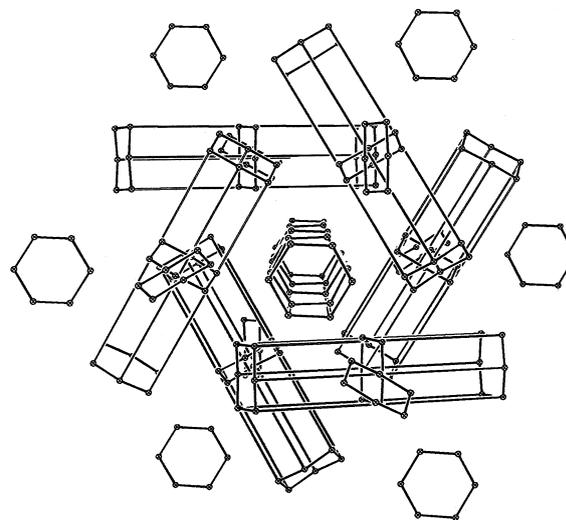


Fig. 5. The cubic unit cell of  $3 \cdot \text{H}_2\text{O}$  with the positions of the Te atoms. The three-dimensional packing of the molecules and the arrangement of the pore-channels is indicated by solid lines connecting the respective  $\text{Te}_6$  hexagons. The view is along the  $[111]$  direction.

gen bonding interactions serve to link the adjacent channels.

The guest water molecules are located in the vicinity of the carbonyl oxygen atoms, *e. g.* in the region between adjoining channels. It has not been possible to locate  $\text{H}_2\text{O}$  hydrogen atoms from final difference Fourier maps, but the respective  $\text{O} \cdots \text{O}$

distances at 2.785 Å between the water molecules and carbonyl oxygen atoms of the five-membered heterocycles suggest the presence of O-H...O=C hydrogen bonding.

Presently, we cannot offer a straightforward explanation for the arene  $\pi$ -stacking in **3**. It may depend on a proper combination of electron-donating and -withdrawing substituents at the aryl ring. It has been demonstrated that withdrawal of  $\pi$ -electron density from aromatic rings by acyl or carboxyl groups weakens  $\pi$ - $\pi$  stacking interactions [12]. In the case of the benzoisochalcogenazoles, this withdrawal of  $\pi$ -electron density may be counterbalanced by electron-donation from the chalcogen atom. For the electron rich tellurium, which has the lowest electronegativity and the highest polarizability among S, Se, and Te, these effects would be maximal. The difference in electron delocalization across the series is also evident from the UV-vis spectra. The spectra reveal that the lowest energy absorption, which may be attributed to a  $n \rightarrow n^*$  transition, is shifted bathochromically from  $\lambda_{\max} = 353$  nm in **1**, to 358 nm in **2**, to 385 nm in **3**.

In conclusion, the crystal structure of the benzoisotellurazole **3** shows a novel three-dimensional network structure capable of inclusion of guest molecules. The assembly of the 3D network depends upon the ability of the heterocycles to form intermolecular  $\pi$ - $\pi$  stacking interactions, which is only observed in the case of the tellurium derivative. The inclusion or adsorption of further guest molecules is now open for an investigation.

## Experimental Section

### Materials and methods

Compounds **1** - **3** were prepared as described in the literature [7]. The absorption spectra were recorded on a Jasco V-570 UV/vis/near IR spectrometer. UV/vis ( $\text{CH}_2\text{Cl}_2$ ,  $c = 10^{-5}$  mol/l):  $\lambda_{\max}(\epsilon) = 353$  nm (4026), 293 (3926), 269 (6859), 262 (6660), 231 (13595) for **1**; 358 (3206), 298 (4026), 277 (6660), 231 (14092) for **2**; 385 (2385), 312 (6387), 290 (6039), 233 (15956) for **3**.

### Collection and reduction of X-ray data

Single crystals of **1**, **2** and **3**· $\text{H}_2\text{O}$  were obtained by recrystallisation from ethyl acetate in the presence of

air. The  $\text{H}_2\text{O}$  molecules in the structure of **3** presumably stem from water traces in the solvent. The crystals were mounted on the tips of glass fibers using perfluoropolyether oil. Intensity data were collected at 180(2) K, using a Bruker CCD X-ray diffractometer. Graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å) was used. The data were processed with SAINT [15] and corrected for absorption using SADABS [16] (transmission factors: 1.00 - 0.56 for **1**, 1.00 - 0.34 for **2**, and 1.00 - 0.76 for **3**). The structures were solved by using the program SHELXS-86 [17]. Refinements were carried out with the program SHELXL-93 [18]. PLATON was used to search for higher symmetry [19], ORTEP-3 for the artwork of the structures [20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and given isotropic thermal parameters 1.2 times (1.5 times for  $\text{CH}_3$  groups) the thermal parameter of the atom to which they were attached.

*Crystal data for 1:*  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ ,  $M_r = 278.36$ , monoclinic, space group  $P2_1/c$  (No. 14),  $T = 180(2)$  K,  $\mu(\text{Mo-}K_\alpha) = 0.22$   $\text{mm}^{-1}$ ,  $a = 9.038(2)$ ,  $b = 16.766(3)$ ,  $c = 19.545(4)$  Å,  $\beta = 100.70(3)^\circ$ ,  $V = 2910(1)$  Å<sup>3</sup>,  $Z = 8$ . 18354 measured reflections, 6918 were unique ( $R_{\text{int}} = 0.1349$ ),  $R_1$ ,  $wR_2 = 0.0540$ , 0.0936 [ $I > 2\sigma(I)$ ],  $R_1$ ,  $wR_2 = 0.1652$ , 0.1209 [all data].

*Crystal data for 2:*  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2\text{Se}$ ,  $M_r = 325.26$ , triclinic, space group  $P\bar{1}$  (No. 2),  $T = 180(2)$  K,  $\mu(\text{Mo-}K_\alpha) = 2.47$   $\text{mm}^{-1}$ ,  $a = 10.141(2)$ ,  $b = 10.660(2)$ ,  $c = 15.026(3)$  Å,  $\alpha = 79.27(3)$ ,  $\beta = 79.34(3)$ ,  $\gamma = 74.31(3)^\circ$ ,  $V = 1520.8(5)$  Å<sup>3</sup>,  $Z = 4$ . 13841 measured reflections, 6947 were unique ( $R_{\text{int}} = 0.0725$ ),  $R_1$ ,  $wR_2 = 0.0526$ , 0.1108 [ $I > 2\sigma(I)$ ],  $R_1$ ,  $wR_2 = 0.0924$ , 0.1242 [all data].

*Crystal data for 3·H<sub>2</sub>O:*  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_3\text{Te}$ ,  $M_r = 391.92$ , cubic, space group  $Ia\bar{3}d$  (No. 230),  $T = 180(2)$  K,  $\mu(\text{Mo-}K_\alpha) = 1.94$   $\text{mm}^{-1}$ ,  $a = 33.297(4)$  Å,  $V = 36916(8)$  Å<sup>3</sup>,  $Z = 96$ . 167609 measured reflections, 3842 were unique ( $R_{\text{int}} = 0.1458$ ),  $R_1$ ,  $wR_2 = 0.0367$ , 0.0809 [ $I > 2\sigma(I)$ ],  $R_1$ ,  $wR_2 = 0.0706$ , 0.0951 [all data]. All non-hydrogen atoms were refined anisotropically except for the oxygen atom of the disordered  $\text{H}_2\text{O}$  molecule.

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