$(B_4Se_7)I_4$: A Molecule with Ufosane-Type Hetero-Cage

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Our recent investigations of ternary rare earth chalcogenoborates were so far successful in the preparation and crystal structure determination of thioborates only [1,2]. Selenoborates could not be synthesized, not even by using high temperature-high pressure techniques. As a consequence, we tried to develop alternative routes by preparing molecular precursors that contain B–Se interconnections and that could be useful for multistep reactions. Boron-chalcogen heterocycles with organic substituents have been at the focus of extensive research in the past [3]. Pointing order to proceed further, we tried to prepare ternary compounds within the systems boron-selenium-halogen, the crystal structures of which had not been investigated before. Recently, we succeeded in the preparation of the previously unknown molecular compound $(B_4Se_7)I_4$ in good yields (95%) by reaction of BI_3 with elemental selenium:

$$4\ BI_3 + 7\ Se \rightarrow (B_4Se_7)I_4 + 8\ I_2$$

In contrast to former reports on the synthesis of yellow $(B_2Se_3)I_2$ by such a type of reaction with the more reactive amorphous red selenium [4], we were able to use gray selenium in the reaction mixture. Excess iodine as well as small amounts of $(B_2Se_3)I_2$ formed as byproducts can be sublimed off in vacuum at 323 K.

Under ambient pressure $(B_4Se_7)I_4$ is a stable compound up to 425 K. By recrystallization of $(B_4Se_7)I_4$ from CS_2 red single crystals of sufficient quality for single-crystal X-ray structure determination are obtained. The extremely air-sensitive compound crystallizes in the tetragonal space group (a = 21.2534(5) Å, c = 7.6982(3) Å, Z = 8, D_x = 4.216 g cm^{-3}). The molecular structure is based on a chiral (B_4Se_7) hetero-cage (Fig. 1), which is topologically equivalent to the ufosane cage with "ideal" point symmetry $D3$, as observed in the crystal structures of $Na_3[P_{11}]$ [5] and $A_3[As_{11}]$ (A = Rb, Cs) [6]. Although topologically equivalent, the Zintl anions $[Pn_{11}]^{3-}$ represent 58 electron systems and there is no strict isoelectronic relationship to the hetero-cage (B_4Se_7): Only in the case that half of the electrons belonging to the B-I single bonds are added to the hetero-cage it would sum up to a total of 58 electrons.

The ufosane-type hetero-cage (B_4Se_7) consists of four boron atoms, three Se_2 units and one isolated selenium atom. The boron atoms complete their tetrahedral coordination by additional bondings to terminal iodine atoms ($B^{[4]=[3Se+1I]}$). The point symmetry of the hetero-cage (as well as of the whole molecule $(B_4(Se_2)_3Se)I_4$) corresponds to $C1$, but is closely related to $C3$ with the pseudo-threefold axis running through B1 and Se1 (see Figs. 1 and 2). An alternative view of the molecule may be focused on the five-membered B_2Se_3 rings forming the cage.

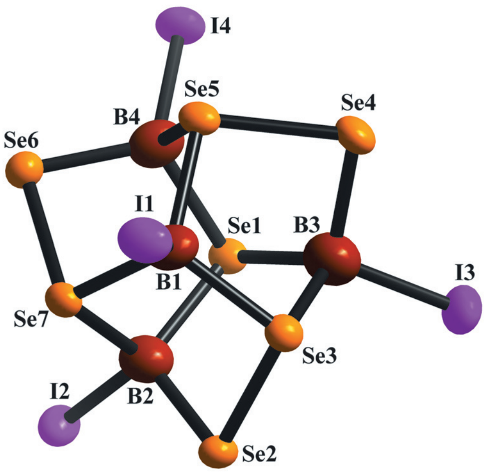


Fig. 1: Molecular structure of $(B_4Se_7)I_4$ with central ufosane-type hetero-cage.

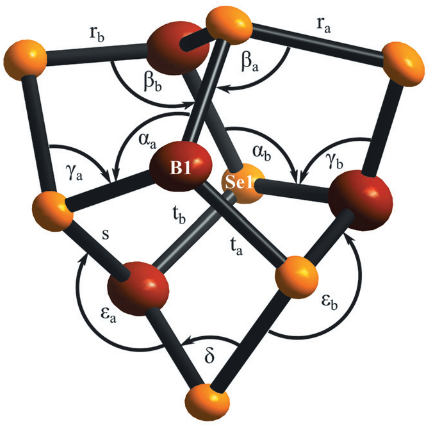
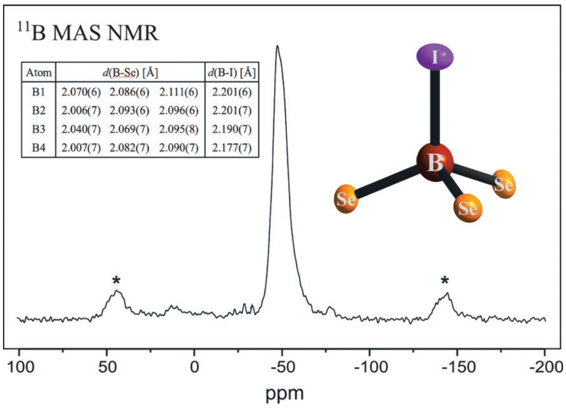


Fig. 2: (B_4Se_7) hetero-cage with notations for distances and angles following the "ideal" point group C3 (see [9]). Respective values are given in Table 1.

Table 1: Intra-molecular bond distances and angles as marked in Figure 2 for the “ideal” point group C3. The “real” symmetry of the molecule, however, corresponds to C1

	distances [Å]		
t_a	2.071(6)	2.086(7)	2.111(6)
t_b	2.094(6)	2.082(6)	2.095(7)
r_a	2.3543(8)	2.354(8)	2.3414(9)
r_b	2.005(6)	2.041(7)	2.007(7)
s	2.067(7)	2.090(7)	2.095(6)
	angles [°]		
α_a (t_a-t_a)	107.9(3)	109.6(3)	107.4(3)
α_b (t_b-t_b)	98.9(2)	99.4(3)	98.6(3)
β_a (t_a-r_a)	99.8(2)	101.5(2)	99.0(2)
β_b (t_b-r_b)	112.8(3)	113.5(2)	112.1(3)
γ_a (t_a-s)	94.7(2)	94.3(3)	95.7(2)
γ_b (t_b-s)	107.3(2)	107.0(3)	107.2(3)
ε_a (s-r_a)	96.3(2)	97.0(2)	97.7(2)
ε_b (s-r_b)	103.9(3)	101.8(3)	100.6(3)
δ (r_a-r_b)	88.7(2)	89.6(2)	90.0(2)



Atom	d(B-Se) [Å]			d(B-I) [Å]
B1	2.070(6)	2.086(6)	2.111(6)	2.201(6)
B2	2.006(7)	2.093(6)	2.096(6)	2.201(7)
B3	2.040(7)	2.069(7)	2.095(8)	2.190(7)
B4	2.007(7)	2.082(7)	2.090(7)	2.177(7)

Fig. 3: ^{11}B MAS NMR of $(B_4Se_7)I_4$ (15 kHz). Spinning sidebands are marked with an asterisk.

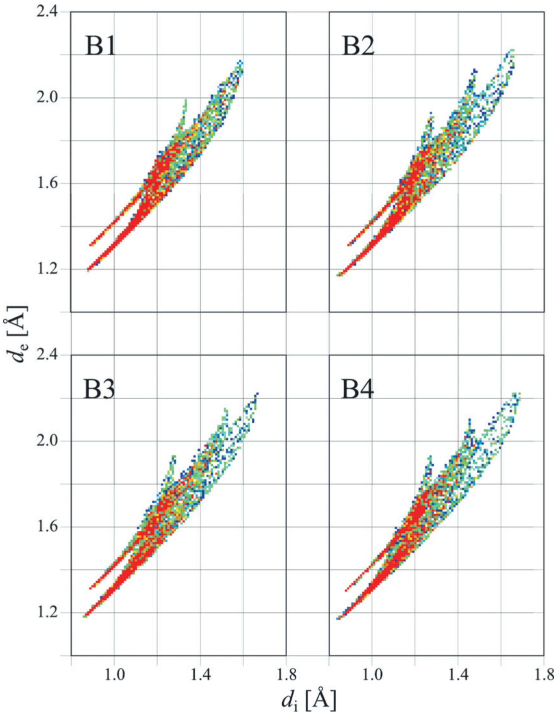


Fig. 4: Fingerprint plots from the Hirshfeld surface analysis of the boron atoms in $(B_4Se_7)I_4$.

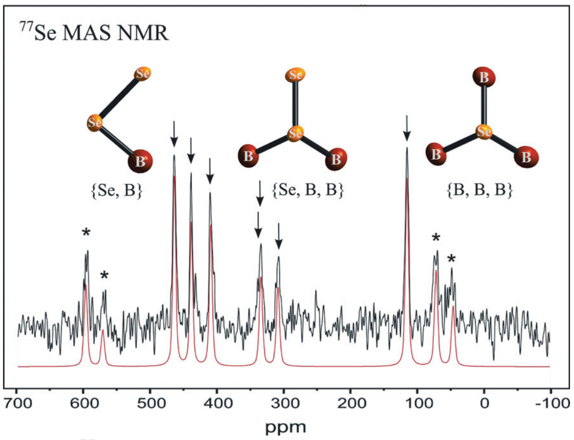


Fig. 5: ^{77}Se MAS NMR of $(B_4Se_7)I_4$ (25 kHz). Spinning sidebands are marked with an asterisk. Black: measured, red: simulated data.

In case of three-fold coordinated boron, as commonly observed for the boron chalcogenidehalides known up to now, these rings are very likely planar [7,8]. The molecule $(B_4Se_7)I_4$, however, is built of non-planar rings with average torsion angles between 37.4° and 45.9°, and ring conformations between envelope and half-chair. Intramolecular bond distances and angles are given in Figure 2 and Table 1. With the exception of the B–Se bonds r_b which are remarkably short, the B–Se bond lenghts are within the range known from related compounds with boron in tetrahedral coordination. Population analyses based on DFT calculations reveal the bond orders for all the intra-molecular contacts being close to unity.

^{11}B MAS NMR spectroscopy does not allow to resolve the NMR signals of the four different boron species with tetrahedral bond topology. The resonance signal shows only moderate asymmetry (Fig. 3). However, fingerprints of the distinct boron atoms from a Hirshfeld surface analysis [10,11] based on the X-ray crystal structure data indicate significant deviations from equivalent local environments at $d_e+d_i > 3.0$ Å (Fig. 4). Obviously, ^{11}B NMR spectroscopy is not sensitive enough to resolve these marginal differences.

In contrast, the ^{77}Se NMR signals of the seven different selenium species, which can be divided into three groups with different bond topology (two bonded {Se, B} and three bonded {Se, B, B}/{B, B, B}) can clearly be distinguished and assigned despite the rather complex signal pattern caused by the various Se–Se couplings (Fig. 5).

In the crystal structure of $(B_4Se_7)I_4$ the molecules are only loosely packed (Fig. 6), a fact that explains the relatively low calculated density of 4.216 g cm^{-3}. The shortest intermolecular contacts (3.7530(7) Å) are observed between iodine atoms I4 and selenium atoms Se4 of neighboring molecules. The shortest intermolecular I–I contacts (d(I1–I3) = 3.9951(6) Å) are in the range of the sum of van der Waals radii.

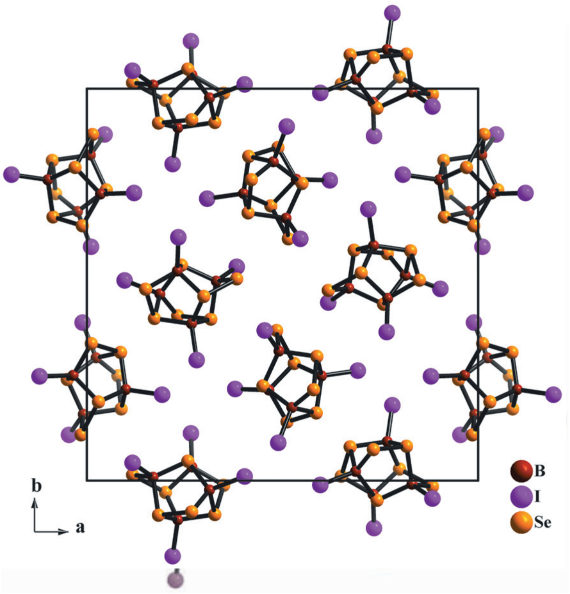


Fig. 6: Packing of the molecules in the crystal structure of $(B_4Se_7)I_4$.

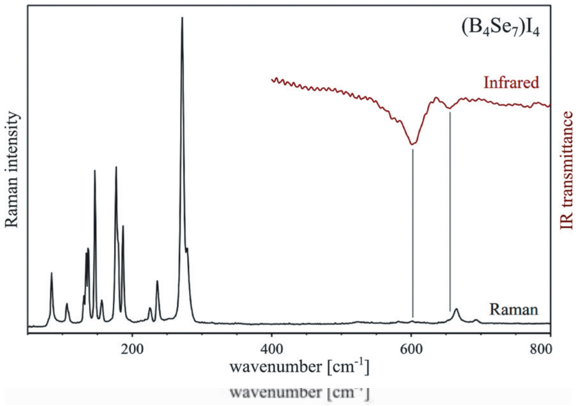


Fig. 7: IR and Raman spectra of $(B_4Se_7)I_4$.

The Raman and IR spectra of $(B_4Se_7)I_4$ (Fig. 7) are in general agreement with the X-ray crystal structure. A visual inspection of the vibrational modes obtained from DFT calculations (TZV(P) level), which resemble the experimental frequencies reasonably well, indicates that most of the internal vibrations are strongly coupled and pure valence and deformation vibrations are not observed. Furthermore, a normal coordinate analysis is hampered by the boron isotope splitting effect (^{10}B – ^{11}B).

The synthesis of $(B_4Se_7)I_4$ is an important step towards the synthesis of new boronselenide networks and ternary metal selenoborates. Our future work will also concentrate on the isolation and crystal structure determination of heterocyclic compounds $(B_2Q_3)X_2$ (Q = S, Se; X = Cl, Br, I) which may open the way to porphyrin-like B_8Q_{16}, as already reported for Q = S [12].

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