

Selenocyanato Derivatives of Hydro-*closo*-borates: Syntheses and Crystal Structures of $(\text{PPh}_4)_2[(\text{SeCN})\text{B}_n\text{H}_{n-1}]$ ($n = 6, 10, 12$)

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The hydro-*closo*-borates $[\text{B}_n\text{H}_n]^{2-}$ ($n = 6, 10, 12$) react with $(\text{SeCN})_2$ in organic media to yield derivatives with one SeCN group bound via Se to the B_n polyhedra. This was verified by single-crystal X-ray structural analysis of the isotypical (P^+) tetraphenylphosphonium salts $(\text{PPh}_4)_2[(\text{SeCN})\text{B}_6\text{H}_5]$ (**1**),

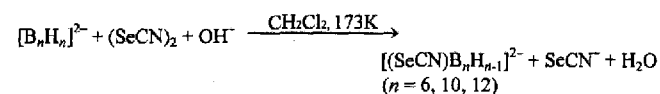
$(\text{PPh}_4)_2[1-(\text{SeCN})\text{B}_{10}\text{H}_9]$ (**2**) and $(\text{PPh}_4)_2[(\text{SeCN})\text{B}_{12}\text{H}_{11}]$ (**3**). The ^{11}B -NMR spectra reveal the features of monosubstituted hydro-*closo*-borates. The ^{77}Se -NMR resonances are observed in the downfield region between $\delta = -22.6$ and -78.8 characteristic of Se-bonded SeCN groups.

The high hydrolytic stability and the interesting bonding character of the *closo*-borates $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ have enabled versatile substitution reactions^[1,2]. However, recently the synthesis of derivatives of the much less stable $[\text{B}_6\text{H}_6]^{2-}$ ion has also been successful^[3-5]. By treatment with halogens, compounds with different degrees of substitution are formed. Some of them were structurally characterized by X-ray diffraction analysis^[7-9]. The analogous reaction of $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ with the pseudohalogen $(\text{SCN})_2$ yields products with one or two thiocyanato groups bound via sulfur^[10-12]. From the *closo*-hexaborate only the monosubstituted and S-bonded compound $[(\text{SCN})\text{B}_6\text{H}_5]^{2-}$ is known^[12] because the further reaction is stopped by protonation of the cluster ion^[5,7]. All mono-, di- and triborates solely form N-bonded compounds with the ambidentate SCN^- ion^[14-16].

In this paper we report the synthesis of monosubstituted selenocyanates $[(\text{SeCN})\text{B}_n\text{H}_{n-1}]^{2-}$ ($n = 6, 10, 12$). In contrast to the well-known N-bonded hydroborates $[\text{BH}_{4-n}(\text{NCSe})_n]^-$ and $[\text{B}_3\text{H}_7(\text{NCSe})]^-$ ^[14,16], only Se-bonded compounds are formed, as confirmed by X-ray diffraction analysis. The new derivatives were characterized by ^{11}B - and ^{77}Se -NMR investigations.

Results and Discussion

Only monosubstituted products were formed by reaction of $[\text{B}_n\text{H}_n]^{2-}$ ($n = 6, 10, 12$) with $(\text{SeCN})_2$ in dichloromethane, even when potassium hydroxide as a strong base was added. Because of the temperature sensitivity of $(\text{SeCN})_2$ and the SeCN substituent, cooling is necessary during the reaction.



It should be emphasized that substitution of $[\text{B}_{10}\text{H}_{10}]^{2-}$ only takes place at an apical boron atom whereas in reactions with halogens^[19] or $(\text{SCN})_2$ ^[11] the preferred position is the B2 atom.

Single crystals suitable for X-ray structure determinations were obtained by slow diffusion of diethyl ether into solutions of **1**, **2** and **3** in acetonitrile. The crystal data parameters are compiled in Table 1. The three compounds crystallize in the same space group $\text{P}\bar{1}$ with similar cell parameters and, as expected, increasing cell volumes from **1** up to **3**. The molecular structures of the dianions with the atomic labelling are shown in Figure 1. The bond lengths within the SeCN groups of all three compounds are comparable and found in the normal range (Table 2). The average Se-C distance of 1.826 Å is significantly lengthened in comparison with the corresponding distance in $(\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3)_2[\text{B}_3\text{H}_7(\text{NCSe})]$ (1.742 Å)^[16]. The B1-Se distances in **1** and **3** are similar [2.029(4), 2.038(3) Å], whereas the analogous bond in **2** [1.987(5) Å] is shorter. With angles of 178.3(4) (**1**), 175.5(5) (**2**) and 175.3(2)° (**3**), the SeCN groups are nearly linear and are positioned above an edge of the B_n cage. The B1-Se bond is inclined to the vertical polyhedral axis with angles of 10.25 (**1**), 5.96 (**2**) and 7.68° (**3**).

The influence of the substituent on the geometry of the boron cages is shown by the increasing distortions from the B_6 up to the B_{12} compound. The distance of *ipso*-B1 to the best basal plane (B2-B5) of **1** is shorter by about 1.8% compared with the distance of the *antipodal* B6 to the corresponding plane. In **2** the upper square pyramid is compressed by 2.1% in comparison with the lower one. The strongest compression, of 4.2%, was observed for the upper pentagonal pyramid of the B_{12} cage. It should be noted that **1** is the first example of a structure of a $[\text{B}_6\text{H}_6]^{2-}$ derivative with an organic cation that is not protonated.

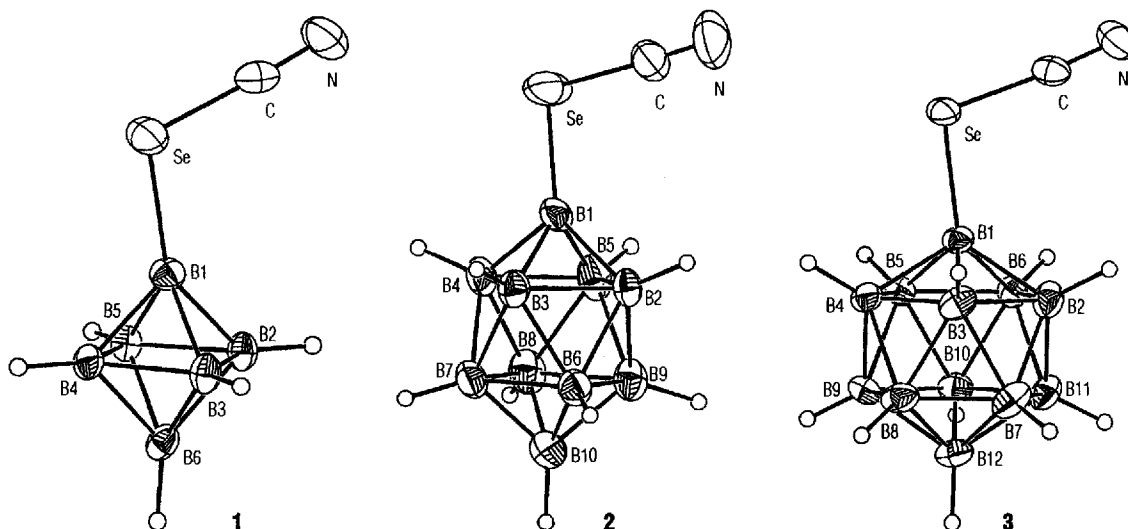
Figure 1. Molecular structures of the dianions of **1**, **2** and **3**; ORTEP^[24], 50% probability ellipsoids

Table 1. Crystal-structure determination: crystal data and experimental data

Compound	1	2	3
Formula	C ₄₉ H ₄₅ B ₆ NP ₂ Se	C ₄₉ H ₄₉ B ₁₀ NP ₂ Se	C ₅₁ H ₅₄ B ₁₂ N ₂ P ₂ Se
Mol. mass	853.62	900.89	965.58
Cryst. system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.527(3)	10.146(2)	10.659(3)
<i>b</i> [Å]	10.906(2)	13.362(2)	11.3039(13)
<i>c</i> [Å]	19.361(2)	19.651(5)	22.399(4)
α [°]	91.37(2)	75.27(2)	87.25(2)
β [°]	92.43(2)	87.04(2)	78.04(2)
γ [°]	103.02(3)	72.07(2)	72.77(2)
<i>V</i> [Å ³]	2162.5(9)	2450.4(9)	2521.4(9)
<i>Z</i>	2	2	2
<i>d</i> _{calcd.} [Mg m ⁻³]	1.311	1.221	1.272
μ [mm ⁻¹]	0.979	0.866	0.846
<i>F</i> (000)	880	928	996
<i>T</i> [K]	173	173	173
2 θ [°]	4–50	4–50	4–50
Refl. collect.	8034	9237	9462
Refl. indep.	7583	8647	8892
Parameter	552	604	642
<i>R</i> 1	0.0530	0.0845	0.0372
<i>wR</i> 2	0.1398	0.2461	0.0908
GOF	1.028	1.065	1.031

The ¹¹B-NMR spectra are consistent with monosubstituted *closo*-borates, showing typical intensity patterns of 4:1:1 (**1**), 1:1:4:4 (**2**) and 1:5:5:1 (**3**) (Table 3). The ¹*J*(B,H) coupling constants are similar and were found in the normal range. The *ipso*-B signals are observed upfield of those of the analogous SCN derivatives, as a result of a smaller *-I* effect and the stronger heavy-atom effect of the Se atom. For the same reason an increasing upfield shift was observed for the series of halogen-substituted *closo*-borates from Cl up to I. The expected splitting of the *ipso*-B1 signal into a quartet due to coupling of ¹¹B (*I* = 3/2) with ⁷⁷Se (*I* = 1/2) could not be resolved.

Table 2. Selected bond lengths (Å) and bond angles (°) of **1**, **2** and **3**

	1	2	3
Se–C	1.830(4)	C–Se	1.815(5)
C–N	1.144(5)	N–C	1.143(7)
B1–Se	2.029(4)	Se–B1	1.987(5)
B1–B2	1.705(5)	B1–B2	1.675(6)
B1–B3	1.714(6)	B1–B3	1.688(6)
B1–B4	1.695(6)	B1–B4	1.680(6)
B1–B5	1.718(5)	B1–B5	1.685(8)
B2–B3	1.733(5)	B2–B3	1.850(6)
B2–B5	1.725(5)	B2–B5	1.841(6)
B2–B6	1.734(6)	B2–B6	1.813(6)
B3–B4	1.744(6)	B2–B9	1.827(7)
B3–B6	1.722(6)	B3–B4	1.853(7)
B4–B5	1.745(5)	B3–B6	1.805(7)
B4–B6	1.730(5)	B3–B7	1.796(7)
B5–B6	1.708(6)	B4–B5	1.843(7)
		B4–B7	1.815(7)
		B4–B8	1.815(7)
		B5–B8	1.816(8)
		B5–B9	1.795(8)
		B6–B7	1.841(7)
		B6–B9	1.836(7)
		B6–B10	1.689(7)
		B7–B8	1.842(7)
		B7–B10	1.692(7)
		B8–B9	1.835(7)
		B8–B10	1.701(8)
		B9–B10	1.704(7)
		B8–B12	1.775(4)
		B9–B10	1.778(4)
		B9–B12	1.770(4)
		B10–B11	1.770(4)
		B10–B12	1.772(4)
		B11–B12	1.776(4)
Se–C–N	178.3(4)	Se–C–N	175.5(5)
B1–Se–C	104.6(2)	B1–Se–C	101.9(2)
Se–B1–B2	143.8(3)	Se–B1–B2	134.4(3)
Se–B1–B3	135.1(3)	Se–B1–B3	127.6(3)
Se–B1–B4	123.7(3)	Se–B1–B4	123.3(3)
Se–B1–B5	132.1(3)	Se–B1–B5	130.6(3)
		Se–B1–B6	125.2(2)

Table 3. ^{11}B NMR: CD_3CN , standard $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$; ^{77}Se NMR: CD_3CN , standard Me_2Se

	^{11}B NMR		^{77}Se NMR	
	δ	$^1J_{\text{BH}}$ [Hz]		δ
1	-12.9, d	130	B2-B5	-72.8
	-14.6, s		B1	
	-17.1, d	129	B6	
2	+2.1, d	150	B10	-68.2
	+0.7, s		B1	
	-25.3, d	130	B2-B5	
	-28.6, d	129	B6-B9	
3	-11.8, s	126	B1	-22.6
	-14.6, d		B2-B6	
	-14.8, d	121	B7-B11	
	-16.6, d	129	B12	
4 ^[a]				-346.8

[a] $(\text{PPh}_4)_2[\text{B}_3\text{H}_7(\text{NCSe})]$.

The ^{77}Se -NMR resonances strongly depend on the bond type of the SeCN substituent. Whereas a singlet at $\delta = -346.8$ was observed for $(\text{PPh}_4)_2[\text{B}_3\text{H}_7(\text{NCSe})]$, with bonding via N, the signals of Se-bonded compounds (**1**), (**2**) and (**3**) were found in the downfield region between $\delta = -22.6$ and -78.8 (Me_2Se as external standard). However, another instructive feature is the coordination of the *ipso*-B atoms. In **1** and **2** they are connected with four neighbouring boron atoms and the ^{77}Se signals appear in a narrow range at $\delta = -72.8$ and -68.2 . In **3**, with the *ipso*-B coordinated to five skeletal B atoms, deshielding evidently occurs, shifting the resonance downfield to $\delta = -22.6$.

The bands in the IR and Raman spectra of **1**, **2**, and **3** exhibit characteristic splittings due to the lowered symmetry compared with the parent compounds. The BH stretching vibrations are found in the range $\tilde{\nu} = 2600\text{--}2400\text{ cm}^{-1}$. The high CN stretching frequencies between $\tilde{\nu} = 2135$ and 2124 cm^{-1} are indicative of bonding of the SeCN substituent via the Se atom. Due to the numerous cation bands, assignment of modes in the framework area below 1100 cm^{-1} is not possible.

The bonding of the ambidentate SeCN^- ion exclusively via the Se atom is strong evidence for the extraordinary properties, described as three-dimensional aromaticity^[17,18], of *closo*-borates. The B atoms become softer due to electron delocalization over the framework. As a result, bonding to the soft Se atom is favoured. For the same reason SCN groups are bound solely via the S atom to the *closo*-borates.

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Experimental

All reactions were carried out in dried solvents. The hydro-*closo*-borates were prepared by standard procedures. – NMR: Bruker AM400, (400 MHz, ^{11}B NMR: 128.38 MHz, ^{77}Se NMR: 76.38 MHz), chemical shifts are referred to $\text{BF}_3 \cdot \text{OEt}_2$ (^{11}B) and Me_2Se (^{77}Se). – IR spectra: Mattson Genesis FT IR. – Raman: IFS 66 FT Bruker. – Melting points: Büchi. – Elemental analyses of the cluster salts with organic cations are difficult to perform due to the formation of boron carbides, and therefore the margins of error for

the C, H and N analyses are large. However, the quality of the crystal structure analysis was so clear as to leave no question regarding the stoichiometry of the compounds.

$(\text{PPh}_4)_2[(\text{SeCN})\text{B}_6\text{H}_5]$ (**1**): A solution of $(\text{SeCN})_2$ prepared by reaction of 1.0 g (2.5 mmol) of $\text{Pb}(\text{SeCN})_2$ with 0.16 g (1.0 mmol) of bromine in 10 ml of dichloromethane is added to a cooled and stirred suspension (-100°C) of 0.5 g of KOH powder and 0.5 g (1.0 mmol) of $(\text{NBu}_4)_2[\text{B}_6\text{H}_6]$ in 30 ml of dichloromethane. After the cooling bath has been removed and the mixture has slowly reached room temperature, the reaction is stopped by addition of a solution of cesium acetate in ethanol. The resulting residue is filtered off and twice washed with ethanol and diethyl ether. The Cs salt is dissolved in 5 ml of a 1 M NaCl solution and separated by preparative IEC on diethylaminoethyl(DEAE)cellulose (1 M NaCl, 20 cm). From the eluent 0.17 g (20%) of yellowish **1** soluble in CH_3CN and CH_2Cl_2 is precipitated by addition of an aqueous solution of $(\text{PPh}_4)\text{Cl}$; m.p. 220°C . – IR: $\tilde{\nu} = 2482$ (s)– 2447 (s) (BH), 2122 (s) (CN), 1500–400 (vs) (cation, BB). – Ra: 3052 (vs) (CH), 2502 (w)– 2438 (w) (BH), 2124 (w) (CN), 1585–200 (cation, BB).

$(\text{PPh}_4)_2[\text{I}-(\text{SeCN})\text{B}_{10}\text{H}_9]$ (**2**): Prepared similarly to **1**. A 0.2 M solution of $(\text{SeCN})_2$ (15 ml) in dichloromethane is added to a cooled suspension (-100°C) of 1 g of KOH and 1.8 g (3.0 mmol) of $(\text{NBu}_4)_2[\text{B}_{10}\text{H}_{10}]$ in 30 ml of dichloromethane. The reaction is stopped at room temperature by adding a solution of 1.0 g $\text{Na}(\text{BPh}_4)$ in 15 ml H_2O . After separation and evaporation of the aqueous phase a colourless residue remains. The Na salt is dissolved in 5 ml of a 2 M NaCl solution and separated by IEC on DEAE (2 M NaCl, 25 cm). By addition of an aqueous solution of $(\text{PPh}_4)\text{Cl}$ to the eluent, colourless **2** is obtained. Yield: 1.4 g of **2** (50%); m.p. 218°C . – IR: $\tilde{\nu} = 2455$ (s) (BH), 2130 (w) (CN), 1500–400 (cation, BB). – Ra: 3059 (vs) (CH), 2513 (w)– 2444 (w) (BH), 2135 (w) (CN), 1585–200 (cation, BB).

$(\text{PPh}_4)_2[(\text{SeCN})\text{B}_{12}\text{H}_{11}]$ (**3**): Preparation and work-up analogous to that for **2**. Starting with 1.9 g (3.0 mmol) of $(\text{NBu}_4)_2[\text{B}_{12}\text{H}_{12}]$, the reaction yields 1.8 g (65%) of colourless **3**; m.p. 218°C . – IR: $\tilde{\nu} = 2490\text{--}2430$ (s) (BH), 2128 (w) (CN), 1500–400 (cation, BB). – Ra: 3066 (vs) (CH), 2519 (w)– 2462 (w) (BH), 2132 (w) (CN), 1585–200 (cation, BB).

Crystal-Structure Determinations: The intensity data were collected with an Enraf-Nonius CAD4 four-circle diffractometer (Mo- K_α radiation, graphite monochromator) and corrected for Lorentz and polarization effects. The structures were solved using direct methods (SHELXS-86^[22]) and refined by full-matrix least-squares techniques based on F^2 (SHELXL-93^[23]). The crystallographic calculations were performed using the program XANADU^[25]. All non-hydrogen atoms except the acetonitrile solvent of **3** were refined anisotropically, whereas the hydrogen atoms of the cations were placed at calculated positions with $d_{\text{CH}} = 0.98\text{ \AA}$. Selected bond lengths and angles are presented in Table 2.

Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405691 (**1**), -405692 (**2**), and -405693 (**3**).

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