Sodium Hydro(isothiocyanato)borates: Synthesis and Structures[‡]

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Dedicated to Prof. Dr. B. Krebs on the occasion of his 65th birthday

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Sodium thiocyanate reacts in THF solution with 18-crown-6 to give the molecular compound Na(18-crown-6)(THF)NCS (**3**) with the N atom of the NCS anion oriented towards Na^+. The same reaction with 15-crown-5 yields the ion pair Na(15-crown-5)NCS (**4**). In contrast, $Na(NCS)(py)_4$, obtained by treating a solution of $Na(H_3BNCS)$ in THF with pyridine, yields $Na(py)_4(NCS)$ (**5**), which has a chain structure with hexacoordinate Na atoms coordinated to five N atoms and an S atom. Na(NCS) in THF adds 1 equiv. of BH_3 to give $Na(H_3BNCS)\cdot n$THF. Addition of 18-crown-6 to this solution yields crystals of the salt $[Na(18\text{-crown-}6)(THF)_2][H_3BNCS]$ (**1**), as shown by X-ray crystallography. Both the cation and the anion show site disorder. However, when 15-crown-5 is used for complexation, the salt $[Na(15\text{-crown-}5)(THF)][H_3BNCS]$ (**2**) can be isolated. Its anion shows an almost linear B–N–C–S unit. Only a mixture of (catecholato)(isothiocyanato)borates results on treating Na(NCS) in THF with catecholborane. However, the borate $Na[catB(NCS)_2]$ is readily formed by adding Na(NCS) to *B*-(isothiocyanato)catecholborane. Single crystals of this compound were obtained as the salt $[Na(18\text{-crown-}6)(THF)_2][catB(NCS)_2]$ (**6**). On the other hand, the reaction of Na(NCS) with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF yields $Na[(9\text{-BBN})NCS)]\cdot n$THF, and, on addition of 18-crown-6, the complex $[Na(18\text{-crown-}6)(THF)_2][(9\text{-BBN})NCS]$ was isolated. Suitable crystals for X-ray structure determination were, however, only obtained by crystallization from tetrahydropyran. This solvate has the rather unusual structure $[Na(18\text{-crown-}6)(thp)_2][\{(9\text{-BBN})NCS\}_2Na(thp)_4]$ (**8**). The sodiate anion has an Na atom coordinated by two S and four O atoms. DFT calculations support these experimental results: The (isothiocyanato)borates are more stable than the thiocyanato isomers. For the latter a bent structure of the B–S–C–N unit with a B–S–C bond angle of 105.7° is predicted.

Introduction

It is well known that the reducing power of alkali metal tetrahydroborates can be influenced by introducing various substituents at the boron atom.[2] In general, there are two routes to these "mixed" hydroborates: (i) reactions of MBH_4 (M = Li, Na, K) with protic reagents HX (X = CN, RCOO, RO), or (ii) addition of the BH_3 component of $H_3B\cdot L$ (L = THF, Me_2S, NR_3) to a nucleophilic anion X^- (X = R, NR_2, OR, CN, NCS). The action of $BH_3\cdot$THF on MSCN was first reported by Aftandilian et al.[3] They concluded from IR data that the BH_3 unit is attached to the S atom of the thiocyanate anion to give $(H_3B{-}SCN)^-$. Klanberg et al.,[4] however, showed that $Li[B(NCS)_4]$ contains isothiocyanate substituents. About 18 years later, Hui analyzed the IR spectra again[5] and came to the conclusion that the adduct of BH_3 with NCS^- is better formulated as the isomer $(H_3B{-}NCS)^-$. Moreover, NMR spectroscopic data also favored the isothiocyanato structure.[6] In order to finally settle the question of isomerism we studied several borate complexes containing the NCS anion by X-ray crystallography.

Results

Crown Ether Complexes of Na(NCS) and $Na(H_3B{-}NCS)$

The compound $Na(H_3B{-}NCS)$, was prepared as shown in Equation (1) and precipitated as the 18-crown-6 solvate **1** by adding the ligand to its THF solution. In previously reported reactions the salt $Na(H_3B{-}NCS)$ was precipitated as a dioxane solvate.[2,4]

$$\text{NaSCN} + BH_3{\cdot}\text{THF} \xrightarrow[\text{THF}]{\text{18-crown-6}} \underset{\mathbf{1}}{\text{Na}(H_3B\text{-NCS})\cdot\text{THF}\cdot\text{18-crown-6}} \qquad (1)$$

Table 1 summarizes some information on the IR data of H_3BNCS^- salts, some of our experimental results as well as results obtained by DFT[7] calculations. In addition IR data for Na(SCN)(15-crown-5) and MeNCS[8] are included.

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Table 1. IR bands [cm^{-1}] reported for $(H_3B{-}NCS)^-$ compared with Na(NCS)(15-crown-5), MeNCS and DFT calculation (for NCS^-)

	Ref.[2]	Ref.[5]	Ref.[5]	**1**	Na(NCS)(14-crown-4)[9]	MeNCS[8]	$(H_3BNCS)^-$, DFT calcd.
νBH	2380−2300	2380, 2330, 2290	2334, 2295, 2260	2365, 2325	–	–	2358, 2355, 2354
νNCS	2175, 2085	2180, 2080	2158, 2055	2172, 2050	2045	2129	2149

We found in most samples of **1** an IR band at 2050 cm^{-1} with different intensities (weak to medium), in addition to a strong band at 2172 cm^{-1}. The band at 2050 cm^{-1} is most likely due to the presence of NCS^-, as can be deduced from the band found at 2045 cm^{-1} observed in Na(NCS)(15-crown-5).[9] In order to make reliable assignments we performed DFT calculations at the B3LYP/6-311**G(d,p) level. There should be two IR-active B−H stretching frequencies at 2355 and 2358 cm^{-1}. Because the calculations were also performed for C_1 symmetry, the degeneracy for ν_{as} (2355 cm^{-1}) is removed, but the third vibration is close to the degenerate band and probably was not resolved experimentally. Moreover, the BH vibrations couple with the CN vibration, for which only one band is predicted at 2149 cm^{-1}, in acceptable agreement with experimental values. The IR data for **1** and MeNCS suggest that the H_3B group is *N*-coordinated to the NCS anion.

Another argument for the presence of a B−N bond in **1** comes from ^{14}N and ^{13}C NMR spectroscopic data. $\delta^{14}N$ for **1** is observed at $\delta = -244$ ppm; the ^{14}N resonance for MeNCS is found at $\delta = -290$ ppm.[10]

The ^{13}C NMR signal is split into a 1:1:1 triplet due to C−N coupling (${}^{1}J_{^{13}\mathrm{C}^{14}\mathrm{N}} = 24$ Hz), which is also found for isocyanides.[11,12] In contrast, the ^{11}B NMR spectroscopic data for **1** ($\delta = -27$ ppm, ${}^{1}J_{^{11}\mathrm{B}^{1}\mathrm{H}} = 96$ Hz) do not allow a distinction between B−N or B−S bonding. For instance, the ^{11}B NMR signal of $(H_3BSH)^-$ is found at $\delta = -25$ ppm[13] and that of $(H_3BNC)^-$ at $\delta = -27$ ppm.[14]

Recrystallization of the 18-crown-6 solvate of $Na(H_3B{-}NCS)$ from THF always caused the formation of Na(NCS)(18-crown-6). This also happened when 15-crown-5 was used. All attempts to obtain single crystals of $Na(H_3B{-}NCS)$(18-crown-6) from THF solutions failed. When crystallization of $Na(H_3B{-}NCS)$ was performed in an excess of $BH_3{\cdot}THF$ in the presence of the 18-crown-6 ligand then suitable crystals for an X-ray structure determination were obtained. However, these showed site disorder for the anion and for THF molecules in the [Na(18-crown-6)$(THF)_2$] cation (see below). In contrast, when 15-crown-5 was used as a ligand then single crystals of compound **2** were obtained without disorder, due to the lower symmetry of the cation [Na(15-crown-5)(THF)]$^+$ [Equation (2)].

$$\mathrm{Na[NCS]} \xrightarrow{+\mathrm{BH_3 \cdot THF}} \mathrm{Na[H_3B\text{-}NCS] \cdot THF} \xrightarrow{+\ 15\text{-crown-5}} \underset{\mathbf{2}}{\mathrm{Na[H_3B\text{-}NCS] \cdot 15\text{-}crown\text{-}5}} \tag{2}$$

In THF solution $Na(H_3B{-}NCS)$ shows a slight tendency to rearrange according to Equation (3). The solutions are fairly stable at room temperature. On heating a 0.1 M solution for 4 d under reflux only 40% of $Na(H_3B{-}NCS)$ decomposed.

$$2\ \mathrm{Na(H_3B{-}NCS)} \rightarrow \mathrm{Na(BH_4)} + \mathrm{Na[H_2B(NCS)_2]} \tag{3}$$

In order to have a solid basis for comparing the IR spectra of the $H_3B{-}NCS$ anion with the Na(NCS) complexes this salt was treated with 18-crown-6 and 15-crown-5 in THF solution; compounds **3** and **4** were isolated as single crystals. On the other hand, when $Na(H_3B{-}NCS)$ was treated in THF solution with an excess of pyridine, crystals of the compound Na(NCS)·4.5py (**5**) were obtained. Thus, pyridine removes the BH_3 group from $Na(H_3B{-}NCS)$ in THF solution.

Na(NCS)(18-crown-6)$(THF)_2$	Na(NCS)(15-crown-5)	Na(NCS)·$(py)_{4.5}$
3	**4**	**5**

Structures

Compounds **3** and **4** are tight ion pairs, with Na coordinated to the N atom of the NCS groups (Figures 1 and 2) while **5** is a coordination polymer with a chain structure in which the Na ions are hexacoordinate, with four py molecules in equatorial positions and an N and S atom of two different NCS anions in *trans* positions (Figure 3). Compound **3** contains an octacoordinate Na ion which sits in the center of the crown ligand. The coordination sphere is completed by a THF molecule and an *N*-bonded NCS anion. In contrast, compound **4** contains a hexacoordinate Na ion, which is present in a distorted pentagonal-pyramidal environment. The Na−N bond lengths increase in the series **3** to **5**. Within the errors of standard deviations one can consider the N−C bond lengths as equal, and this holds also for the C−S bond lengths. The average Na−O distance in **3** is significantly longer than in **4**, while the Na−O distance to the THF molecule in **3** is about 0.3 Å shorter than the distances to the O atoms of the crown ether. Selected molecular parameters are summarized in Table 2, others are found in the captions to the figures.

The trihydro(isothiocyanato)borate **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$. The compound is ionic with formula [Na(18-crown-6)$(THF)_2$]$^+$[$H_3B{-}NCS$]$^-$ (see Figure 4). Because the Na ion occupies a crystallographic

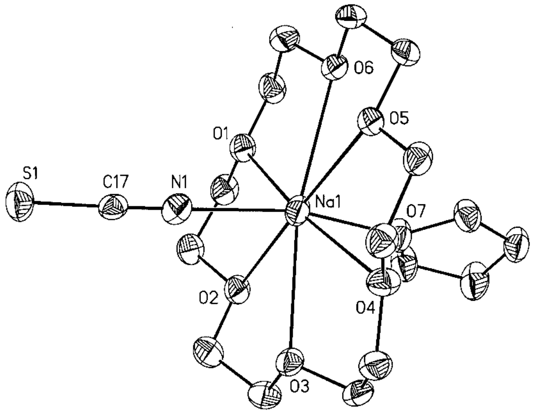


Figure 1. Molecular structure of Na(NCS)(18crown-6)(THF)$_2$ (**3**) (ORTEP); selected bond lengths [Å]: N1−C17 1.156(3), C17−S1 1.635(3), Na1−N1 2.375(3), Na1−O1 2.439(2), Na1−O2 2.756(2), Na1−O3 2.781(2), Na1−O4 2.760(2), Na1−O5 2.779(2), Na1−O6 2.814(2), Na1−O7 2.419(2); selected bond angles [°]: Na1−N1−C17 175.9(2), N1−C17−S1 178.2(2), O1−Na1−O2 62.71(6), O2−Na1−O3 60.45(6), O3−Na1−O4 59.76(5), O4−Na1−O5 59.47(6), O5−Na1−O6 58.99(6), O6−Na1−O1 61.53(6), O1−Na1−O7 90.15(8), O2−Na1−O7 81.80(6), O3−Na1−O7 85.25(7), O4−Na1−O7 82.71(7), O5−Na1−O7 97.16(6), O6−Na1−O7 83.91(7), N1−Na1−O1 87.36(7), N1−Na1−O2 85−07(7), N1−Na1−O3 84.81(8), N1−Na1−O4 100.34(9), N1−Na1−O5 85.87(8), N1−Na1−O6 106.61(7), N1−Na1−O7 166.27(8)

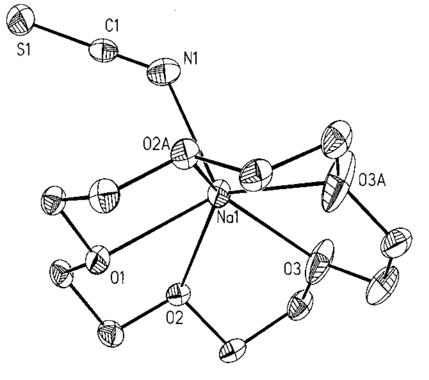


Figure 2. Molecular structure of Na(NCS)(15-crown-5) (**4**) (ORTEP); selected bond lengths [Å] (see also Table 1): Na1−O1 2.369(4), Na1−O2 2.461(3), Na1−O3 2.356(4), O1−C2 1.426(4), O2−C3 1.421(4), O2−C4 1.426(4), O3−C5 1.411(5), O3−C6 1.344(5); selected bond angles [°]: C1−N1−Na1 133.6(5), N1−Na1−O1 94.5 (2), N1−Na1−O3 121.3(2), N1−Na1−O2 97.13(9), O1−Na1−O3 127.3(2), O2−Na1−O3A 132.8(2), O2−Na1−O2A 136.5(1), O3−Na1−O2A 132.8(1)

inversion center the THF molecules are present in *trans* positions. The structure of this cation has been observed already in several [Na(18-crown-6)(THF)$_2$]$^+$ complexes with various anions.[15−18] Moreover, the two orientations of the anion result from a crystallographic inversion center in the middle of the two N−C bonds (equal 1:1 occupancy). Therefore, there are large errors regarding the bond lengths of the linear B−N−C−S unit.

In contrast, no disorder problem was associated with compound **2**, which is also ionic. It crystallizes in the orthorhombic space group $P2_12_12_1$. Figure 5 shows the two ions. The cation closely resembles compound **4** whose NCS ligand has been replaced by a THF molecule. The

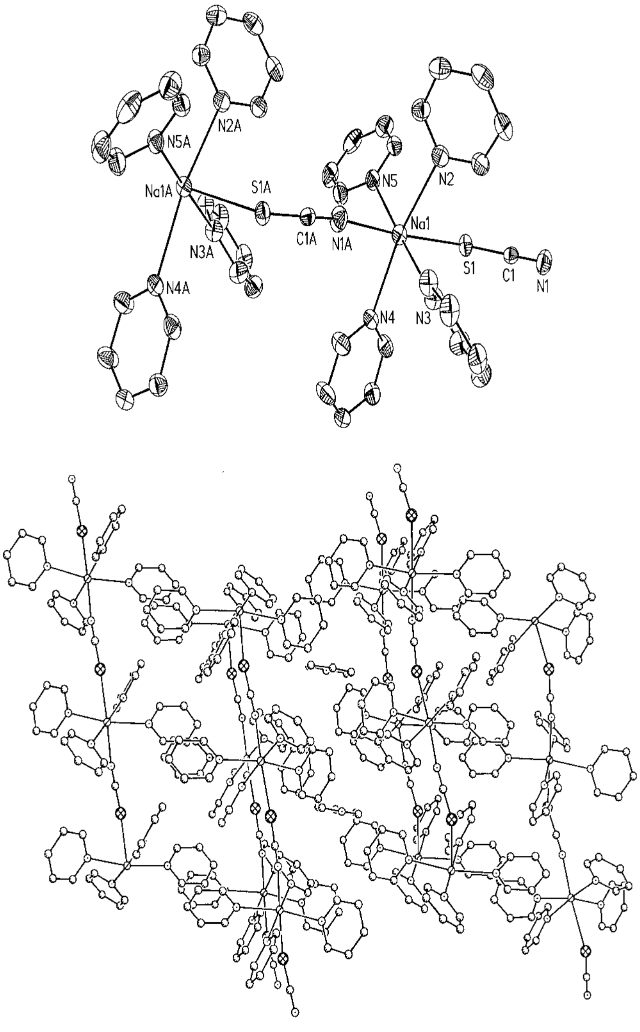


Figure 3. (top) Part of the chain structure of Na(NCS)·4py (ORTEP); solvent of crystallization has been omitted for clarity; selected bond lengths [Å]: Na1−N1A 2.417(3), Na1−S1 3.603(1), S1−C1 1.639(3), C1−N1 1.151(3), Na1−N2 2.519(2), Na1−N3 2.505(2), Na1−N4 2.521(2), Na1−N5 2.483(2), N2−C2 1.328(3), N2−C6 1.324(3), N3−C7 1.326(3), N3−C11 1.328(3), N4−C12 1.320(3), N4−C16 1.331(3), N5−C17 1.328(3), N5−C21 1.321(3); selected bond angles [°]: Na1−S1−C1 116.25(9), S1−C1−N1 178.4(2), N2−Na1−N3 84.69(8), N3−Na1−N4 87.03(7), N4−Na1−N5 91.69(7), N5−Na1−N2 96.13(8), N2−Na1−N4 170.20(8), N3−Na1−N5 175.21(8), N2−Na1−S1 88.45(6), N3−Na1−S1 94.92(7), N4−Na1−S1 87.03(6), N5−Na1−S1 80.40(6), S1−Na1−N1A 172.80(7), N1A−Na1−N4 92.67(8), C2−N2−C6 117.1(2), C7−N3−C11 116.6(2), C12−N4−C16 115.1(2), C17−N5−C21 116.3(2); (bottom) view down the *b* axis of the unit cell of **5**

Table 2. Selected bonding parameters of Na(NCS) solvates **3**−**5**

	3	**4**	**5**
Space group	$P2_1/c$	$Pmn2_1$	$I2/a$
Na1−N1	2.375(3)	2.393(5)	2.417(3)
N1−C1	1.156(3)	1.170(8)	1.151(3)
C1−S1	1.635(3)	1.633(7)	1.639(3)
Na1−N1−C1	175.9(2)	133.6(5)	173.6(2)
N1−C1−S1	178.2(2)	179.3(5)	178.4(2)
Na1−S1−C1	−	−	116.3(2)

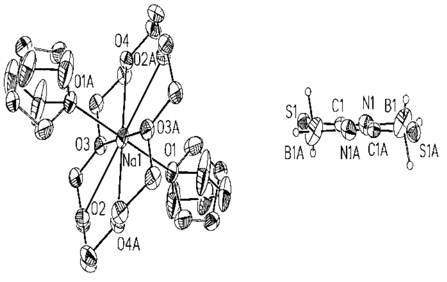


Figure 4. Molecular structure of [Na(18-crown-6)(THF)$_2$][H_3B-NCS] showing the two orientations of the anion; only the parameters for the cation are given; selected bond lengths [Å]: Na1−O1 2.320(2), Na1−O2 2.818(2), Na1−O3 1.719 (1), Na1−O4 2.777(1); selected bond angles [°]: O1−Na1−O2 94.99(6), O1−Na1−O3 88.75(6), O1−Na1−O4 95.44(6), O2−Na1−O3 60.15(9), O2−Na1−O3 60.15(4), O3−Na1−O4 61.37(5), O2−Na1−O3A 119.85(4), O3−Na1−O4A 118.63(5); due to the inversion center at Na1 the THF molecules are site disordered (SOF = 0.5; both orientations are shown)

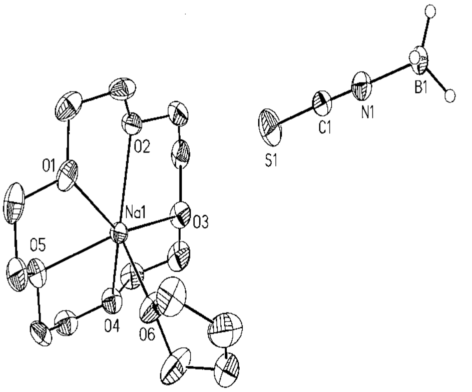


Figure 5. Molecular structure of [Na(15-crown-5)(THF)][H_3B-NCS] (**2**); selected bond lengths [Å]: B1−N1 1.609(7), N1−C1 1.154(6), C1−S1 1.603(6), Na1−O1 2.384(4), Na1−O2 2.375(4), Na1−O3 2.371(4), Na1−O4 2.361(4), Na1−O5 2.366(4), Na1−O6 3.031 (7), O1−C2 1.437(8), O2−C4 1.396(7), O2−C3 1.412(7), O3−C5 1.435(7), O3−C6 1.430(8), O4−C7 1.455(8), O4−C8 1.423(9), O5−C9 1.449(7), O5−C10 1.412(8), O6−C12 1.417(8), O6−C15 1. 426(8), C−C(crown) 1.45(1) to 1.503(9); selected bond angles [°]: B1−N1−C1 179.1(6), N1−C1−S1 178.6(7), O1−Na1−O2 70.0(2), O1−Na1−O3 136.3(2), O1−Na−O5 71.0(2), O2−Na1−O3 70.7(2), O2−Na1−O4 140.5(2), O2−Na1−O5 124.7(2), O2−Na1−O6 95.9(2), O3−Na1−O4 70.4(2), O3−Na1−O5 119.1(2), O3−Na1−O6 96.92(2), O4−Na1−O5 70.5(2), O4−Na1−O6 95.6(2), O5−Na1−O6 131.6(2), C2−O1−C11 114.4(6), C3−O2−C4 115.8(5), C5−O3−C6 114.2(5), C7−O4−C8 115.8(5), C9−O5−C10 114.2(5), C12−O6−C15 105.3(6)

H_3B-NCS anion has an almost linear B−N−C−S skeleton [bond angles B−N−C = 178.7(4)° and N−C−S = 178.9(4)°]. The B−N bond is comparatively long [1.575(5) Å] for a tetrahedral boron atom bound to a two-coordinate N atom. On the other hand, the C−N bond is very short [1.150(5) Å], and corresponds to a C−N triple bond. However, the short C−S bond [1.613(4) Å] is indicative of a double bond. With these structure determinations it is proved that the reaction of borane·THF with Na(NCS) results exclusively in formation of the trihydro(isothiocyanato)borate anion. This seems logical considering the strengths of the B−N and B−S bonds.

Calculations

In order to support the experimental bonding parameters of the [H_3B-NCS]$^-$ ion we performed MO calculations on this anion at the B3LYP and MP2(fc) level of theory with the basis set 6-311++G(d,p). These calculations were started with C_1 symmetry for the anion as found experimentally (however, it should be noted that the determined B−H bond lengths have high e.s.d.s), but resulted in C_{3v} symmetry for both methods. Table 3 shows the calculated values; it also contains the experimental data.

Except for the C−S bond lengths all data are in good agreement with those found for compound **2**. Due to the disorder in the anion of compound **1** as well as of [Bu_4N][H_3B-NCS][6] these data are too inaccurate to use them for comparison.

In order to also obtain information on the structure of the isomeric trihydro(thiocyanato)borate and its stability we performed analogous calculations for [H_3B-SCN]$^-$ (see Table 4). One can see that the C−N bond length is practically the same whether the BH_3 group is *N*- or *S*-coordinated but the C−S bond is to be expected to be longer in the trihydro(thiocyanato)borate than in the trihydro(isothiocyanato)borate. More importantly, the B−S−C−N unit is not linear, and a B−S−C bond angle of about 104° is to be expected. In each case the trihydro(isothiocyanato)borate is more stable than its isomer by −27 kJ/mol or −57 kJ/mol, respectively, depending on the level of theory (Table 4). This is reflected also in the calculation of the reaction energies as shown in Equations (4)−(6).

$$BH_3\cdot THF + NCS^- \rightarrow H_3B-NCS^- + THF;\ \Delta E = -96\ kJ \qquad (4)$$

$$BH_3\cdot THF + SCN^- \rightarrow H_3B-SCN^- + THF;\ \Delta E = -38\ kJ \qquad (5)$$

$$2\ BH_3\cdot THF + NCS^- \rightarrow H_3B-NCS-BH_3^- + 2\ THF;\ \Delta E = -109\ kJ \qquad (6)$$

All these reactions are exothermic. The trihydro(thiocyanato)borate is less favored. However, a thiocyanatobis(trihydroborate) [Equation (6)] should also be stable but we were unable to detect this anion, even in concentrated solutions.

Further (Isothiocyanato)borates

In principle, many more (isothiocyanato)borates may be accessible simply by addition of NCS$^-$ as nucleophile to a sufficiently Lewis-acidic boron center. We have studied two of them. In the first case we allowed catecholborane, catBH, to react with Na(NCS), and in the second case we used 9-borabicyclo[3.3.1]nonane (9-BBN).

The ^{11}B NMR spectra recorded for the reaction mixture of catecholborane with Na(NCS) revealed that several borate anions are formed. Table 5 shows the product distribution. We could not separate the mixture by fractional crystallization or separate Na[catB(NCS)$_2$] (**6**) by adding di-

Table 3. Calculated and experimental bond lengths [Å] and bond angles [°] for H_3B-NCS^-

	MP2(fc)/6-311**G(d,p)	B3LYP/6-311**G(d,p)	**2**	**1**	$[Bu_4N][H_3B-NCS]$[6]
B−N	1.560	1.648	1.575(5)	1.54(2)	1.81(2)
N−C	1.185	1.168	1.150(5)	1.09(2)	1.143(4)
C−S	1.631	1.641	1.613(4)	1.66(3)	1.661(4)
S−C−N	180.0	180.0	178.9	178(1)	179.4(3)
C−N−B	180.0	180.0	178.7(4)	176(2)	179.1(8)

Table 4. Calculated bond lengths [Å]and bond angles [°]for H_3B-SCN^-

	MP2(fc)/6-311**G(d,p)	B3LYP/6-311**G(d,p)
B−S	1.992	2.044
N−C	1.187	1.167
C−S	1.679	1.687
S−C−N	177.4	177.2
C−S−B	103.0	105.7
ΔE (to H_3B-NCS^-)	+27 kJ/mol	+57 kJ/mol

Table 5. Product distribution resulting in the reaction of catecholborane with Na(NCS) in THF monitored by ^{11}B NMR spectroscopy

	δ^{11}B [ppm]; $^{1}J_{B,H}$ [Hz]	Amount
catBH	23.0 (d); 190	7%
$Na[B(cat)_2]$	12.3 (s)	58%
$Na[catB(NCS)_2]$	−0.1 (quint); 24 $^{1}J_{B,N}$	8%
$Na[H_2B(NCS)_2]$	−19.5 (t); 115	27%

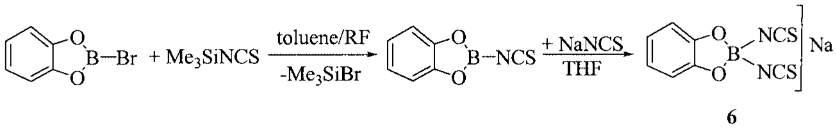
oxane. There is, however, an unusual feature in the proton-decoupled ^{11}B NMR spectrum of the products formed in solution, because the quintuplet at $\delta = -0.1$ ppm does not vanish. Therefore, this signal excludes the presence of B−H bonds. Moreover, the chemical shift excludes a BH_4 anion ($\delta^{11}B = -41$ ppm).[19] This is also revealed by the fact that the intensity of the five signals is 1:2:3:2:1 while BH_4^- requires a 1:4:6:4:1 intensity. However, the observed coupling pattern corresponds to the coupling of the boron nucleus with two nuclei of spin $I = 1$. Therefore, the observed coupling is due to $^{1}J_{^{11}B^{14}N}$. Such a coupling has already been detected for ^{15}N-enriched (isothiocyanato)borates $B(NCS)_{4-n}X_n^-$ (X = F, Cl; n = 1, 2, 3)[20] which have, however, not been isolated as alkali metal salts. The observed coupling constant $^{1}J_{^{11}B^{14}N}$ corresponds to those found for these species (21−28 Hz). Usually it is difficult to observe $^{1}J_{^{11}B^{14}N}$ couplings because of rapid quadrupole relaxation as both nuclei have strong quadrupole moments which generally leads to broad unresolved signals. For instance, no such coupling is observed for diazido(catecholato)borate whose structure is very similar to that of **6**.[21]

The synthesis of pure sodium catecholatobis(isothiocyanato)borate can be readily achieved by the reaction sequence shown in Equation (7).

Compound **6** not only shows a well-resolved 1:2:3:2:1 quintuplet in the ^{11}B NMR spectrum but also a 1:1:1:1 quadruplet in the ^{14}N NMR spectrum. Moreover, in concentrated THF solutions of **6** the ^{13}C resonance for the isothiocyanato group can also be detected as a broad signal at $\delta = 131$ ppm.

Single crystals of **6** separated from the THF solution after addition of 18-crown-6. They have the composition $[Na(18\text{-crown-}6)(THF)_2][catB(NCS)_2]$. The crystals are triclinic, space group $P\bar{1}$, $Z = 2$. Figure 6 shows the structures of the two ions. The anion has almost C_{2v} symmetry, which by calculation is shown to be an energy minimum.

Table 6 contains selected experimentally determined and calculated data for the $[catB(NCS)_2]$ anion. There is good agreement between both except that the experimentally determined B−N−C bond angle is 12.3° smaller than calculated. The N−B bonds are shorter than in (H_3B-NCS). Moreover, the C−S bond is shorter than in free NCS^- (0.04 Å) and shorter by 0.023 Å than in $(H_3B-NCS)^-$. The calculated vibrational frequencies fit well with experimental values if multiplied by a factor of 0.96.[22] Calculation predicts 2150 cm^{-1} for the A_1 vibration of the NCS group and 2112 cm^{-1} for the B_1 vibration. These were found in the IR spectrum at 2150 and 2115 cm^{-1} and in the Raman spectrum at 2144 and 2108 cm^{-1}, respectively.



6

(7)

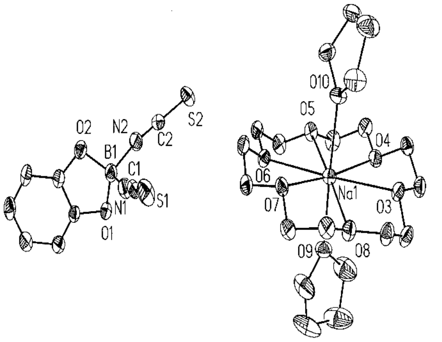


Figure 6. Structure of [Na(18-crown-6)(THF)$_2$][B(cat)(NCS)$_2$] (**6**); selected bond lengths [Å]: B1−O1 1.452(4), B1−O2 1.447(4), B1−N1 1.551(4), B1−N2 1.535(5), N1−C1 1.164(4), N2−C2 1.161(4), C1−S1 1.593(4), C2−S2 1.587(4), O2−C3 1.368(4), O2−C8 1.373(4), C3−C8 1.393(4), Na1−O3 2.697(2), Na1−O4 2.835(2), Na1−O5 2.906(2), Na1−O6 2.704(2), Na1−O7 2.703(2), Na−O8 2.672(2), Na1−O9 2.307(2), Na1−O10 2.305(2), O3−C9 1.410(4), O3−C20 1.432(3), O5−C12 1.420(4), O5−C13 1.412(4), O6−C14 1.418(4), O6−C15 1.420(3), O7−C16 1.420(4), O7−C17 1.432(3), O8−C18 1.424(3), O8−C19 1.424(4), O9−C10 1.484(4), O9−C21 1.409[(5), O10−C25 1.423(4), O10−C28 1.410(4); selected bond angles [°]: O3−Na1−O4 60.65(6), O4−Na1−O5 60.65(6), O5−Na1−O6 59.70(6), O6−Na1−O7 62.10(6), O7−Na1−O8 61.34(6), O8−Na1−O3 61.38(6), O3−Na1−O10 86.53(8), O4−Na1−O10 87.71(8), O5−Na1−O10 83.78(7), O6−Na1−O10 91.72(8), O7−Na1−O10 87.25(8), O8−Na1−O10 101.12(8), O9−Na1−O10 170.9(1), O1−B1−O2 107.9(3), N1−B1−N2 104.8(3), B1−N1−C1 163.0(3), B1−N2−C2 166.9(3)

Table 6. Experimental and calculated bond lengths [Å] and bond angles [°] of the anion [catB(NCS)$_2$]$^-$

	Experimental data	Calculated data[a]
B−O	1.465(4)	1.482
B−N	1.543(5)	1.527
N−C	1.163(4)	1.174
C−S	1.590(4)	1.614
O−B−O	107.9(3)	105.3
N−B−N	104.8(3)	107.8
B−N−C	163.0(3), 166.9(3)	177.3
N−C−S	177.8(3), 178.8(3)	178.6

[a] B3LYP/6-311*G(d) level of theory.

When Na(NCS) is treated with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF, the solution shows a single doublet in the ^{11}B NMR spectrum at $\delta = -11.4$ ppm, $^1J_{^{11}B^1H} = 100$ Hz. This is compatible with the presence of an *N*-bonded NCS anion in Na[(9-BBN)NCS] (**7**).

Addition of 18-crown-6 to the solution of **7** precipitates the crown ether complex, which, after drying followed by dissolution in THF, leads to two ^{11}B NMR signals at $\delta = -6.3$ and 31.0 ppm. None of them shows any multiplicity due to B,H coupling. The signal at $\delta = 31.0$ ppm may be due to a 9-BBN(NCS)·THF solvate [9-BBN(NMe$_2$): $\delta^{11}_B = 47.7$ ppm;[23] Ph$_2$BBr·OEt$_2$: $\delta^{11}_B = 33.4$ ppm[24]] and the latter could be due to its dimer. But this interpretation is speculative.

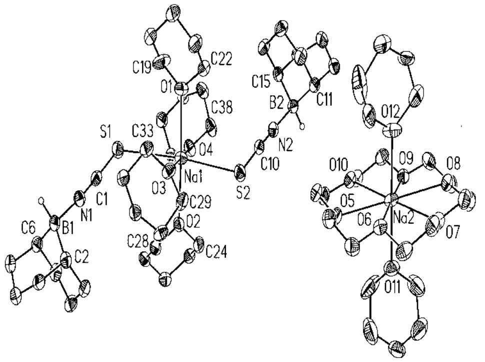


Figure 7. Structure of [Na(18-crown-6)(thp)$_2$][Na(thp)$_4${(9-BBN)NCS}$_2$] (**8**); selected bond lengths [Å]: N1−C1 1.168(5), N2−C10 1.166(5), C1−S1 1.563(6), S2−C10 1.595(6), B1−N1 1.564(7), B2−N2 1.568(7), Na1−S1 3.254(2), Na1−S2 3.034(2), Na1−O1 2.377(3), Na1−O2 2.329(3), Na1−O3 2.302(3), Na1−O4 2.322(3), B1−C2 1.617(7), B1−C6 1.609(6), B2−C11 1.596(6), B2−C15 1.607(6); selected bond angles [°]: B1−N1−C1 174.7(4), N1−C1−S1 177.8(4), B2−N2−C10 175.1(4), N2−C10−S1 178.2(4), O1−Na1−O2 177.4(1), O1−Na1−O3 89.2(1), O1−Na1−O4 92.6(1), O2−Na1−O3 90.7(1), O2−Na1−O4 87.4(1), O3−Na1−O4 176.4(1), S1−Na1−O1 87.93(9), S1−Na1−O2 89.46(9), S1−Na1−O3 89.46(9), S1−Na1−O4 87.43(9), S2−Na1−O1 95.6(1), S2−Na1−O2 96.60(9), S2−Na1−O3 86.38(9), S2−Na1−O4 96.60(9), N1−B1−C2 111.8(4), N1−B1−C6 110.0(4), N2−B2−C11 109.2(4), N2−B2−C15 110.2(4), C2−B1−C6 105.7(4), C1−B2−C15 106.9(4); data for the cation [Na(18-crown-6)(thp)$_2$]; selected bond lengths [Å]: Na2−O5 2.733(3), Na2−O6 2.690(4), Na2−O7 2.707(3), Na2−O8 2.819(3), Na2−O10 2.682(3), Na2−O11 2.342(4), Na2−O12 2.364(4); selected bond angles [°]: O5−Na2−O6 60.4(1), O6−Na2−O7 61.7(1), O7−Na2−O10 177.3, O11−Na2−O12 176.4(1), O6−Na2−O10 121.1(1)

The crown ether complex of **7** can be crystallized from THF solution. Its crystals have the composition Na(18-crown-6)(THF)$_2$[(9-BBN)NCS]. Although a good data set could be collected for the monoclinic crystals, the structure could not be resolved satisfactorily. However, crystallization of **7** from tetrahydropyran (thp) produced single crystals of [Na(18-crown-6)(thp)$_3$][(9-BBN)NCS] which proved to be [Na(18-crown-6)(thp)$_2$][Na(thp)$_4${(9-BBN)NCS}$_2$] (**8**) in the solid state. As shown in Figure 7 the cation is similar in structure to [Na(18-crown-6)(THF)$_2$]$^+$ [15−18] with two thp molecules in *trans* positions. In the anionic part of the compound the sodium cation is surrounded by four thp molecules and two sulfur atoms which are supplied by two (9-BBN)NCS anions. The S1−Na1−S2 bond angle is 174.47(6)°, and the O1−Na1−O2 and O3−Na1−O4 bond angles are 177.4(1) and 176.4(1)°, respectively. This results in an averaged S1−Na1−O bond angle of 88.5°, and an averaged S2−Na1−O bond angle of 91.5°. Interestingly, the two Na−S bond lengths are significantly different, with Na1−S1 3.254(2) and Na1−S2 3.045(2) Å. Also, the Na−O bonds differ, spanning a range from 2.302(3) to 2.377(3) Å. However, the bonding parameters for the two 9-BBN units are rather similar as shown, for instance, by the two B−N bond lengths, which are 1.564(5) and 1.568(5) Å.

Discussion

It is now well established from previous results and those presented here that the NCS$^-$ anion coordinates to the boron atom of BH_3 through its N atom. Although this was already deduced from spectroscopic data[3−5] this is now ascertained by X-ray structural results for the solid state. From a chemical point of view this seems logical because the B−N bond is much stronger than the B−S bond; therefore, (isothiocyanato)borates should be favored over (thiocyanato)borates, and this is supported by DFT calculations. This argument is valid also for borane derivatives.

In general, the addition of the NCS$^-$ anion to a borane unit (BH_3, catecholborane, 9-BBN) is not necessarily the best preparative route, in particular not for BH_3 and catecholborane because the (isothiocyanato)borates formed can react with the borane by hydrogen exchange giving rise ultimately to the formation of tetrahydroborate. This kind of behavior is particularly noticeable for reactions of alkali metal alkoxides with BH_3 in THF,[7] but also for catecholborane, which, on addition of a nucleophile, gives an organyloxoborate in analogy to the BH_3/OR^- reaction. In the case of 9-BBN we did not observe this behavior: there was a straightforward reaction to the borate **7** without any by-products. Most likely this is due to the bulky R_2B group of the 9-borabicyclo[3.3.1]nonyl group.

The ligand distribution reaction can be retarded or even prevented when an (isothiocyanato)borane is treated with NCS$^-$ as shown for (isothiocyanato)catecholborane, which leads to the bis(isothiocyanato)borate **6**.

Although a series of (isothiocyanato)borates $B(NCS)_{4-n}X_n^-$ is known,[19] no crystal structures of their salts have been reported. This is also the case for the (thiocyanato)hexaborate $B_6H_5(SCN)^{2-}$ where it is deduced from vibrational spectroscopy that the NCS group is *S*-bonded.[25] In $B_6H_5(SeCN)^{2-}$ the presence of the B−Se bond has been established.[26] Obviously the B_6H_5 unit acts as a soft acid.

On average, the B−N bonds of the (isothiocyanato)borates are longer [1.542(5)−1.575(5) Å] than in tetrakis(dihydropyridino)borate [1.546(2) Å].[27] One would have expected the opposite because the N atom of the isothiocyanate ion is sp-hybridized while in the (dihydropyridinato)borate the N atom resides in a planar environment and, therefore, is sp^2-hybridized. Obviously the B−N bond of the investigated (isothiocyanato)borates is weaker than in the aminoborate derivative.

While crown ether complexes of the alkali metal thiocyanates have been investigated in the early days of the polyether complexes[28] the only compound which is akin to **4** is the dicyclohexano-15-crown-5 complex of Na(NCS) whose bonding parameters resemble those of **4**.[29] As shown, the two crown ether complexes **3** and **4** have molecular structures. In the case of the 18-crown-6 complex the sodium ion is octacoordinate. The Na−N bond is shorter than the Na−O bond to the coordinated THF molecule while all bonds to the O atoms of the crown are more than 0.3 Å longer. On the other hand, in the crown ether compound **4** the Na−N bond is somewhat longer than in complex **3** in spite of the fact that the sodium ion is only hexacoordinate, and has the geometry of a distorted pentagonal pyramid; the Na−N bond in [Na(15-crown-5)(NCMe)]$^+$ is even longer.[29] Moreover, the crown ether in this cation is less symmetrically bonded than in **4**, which has a mirror plane through the atoms S, C, N, Na and O1. In contrast, the hexacoordinate Na ion in the pyridine complex **5** approaches an octahedral geometry. Moreover, the Na−N bond in the acetonitrile adduct [2.960(7) Å] is longer than in **4**. This is not unusual. The Na−N bond of the NaNCMe unit is even longer than in **4** and only about 0.1 Å shorter than the Na−N bonds to the pyridine molecules. In this case the octahedral coordination site is filled by a sulfur atom, and this leads to a zig-zag arrangement of the building blocks. Na−S bonds are also present in the anion of **8**. In this case, the NCS anion behaves similarly to the pyridine complex of Na(SCN) except for the fact that in **5** each Na ion is *N*- and *S*-coordinated as a consequence of the *B*-bonded NCS group in **8**. From this point of view it is surprising that there is no Na−S coordination in compounds **1** and **2** nor in the 18-crown-6·THF complex of **6** where the S atom of the *B*-bonded NCS anion is not able to replace a THF molecule coordinated to Na.

In the anion of the catecholatoborate **6** both the O−B−O and the N−B−N bond angles are smaller than the ideal tetrahedral bond angle. However, in the bis(catecholato)borate anion the O−B−O bond angles are even more acute by 3°.[30] Moreover, the B−O bonds in **6** are shorter than those found for comparable (catecholato)boranes such as catecholborane−oxazolidine [B−O, 1.479(2), 1.481(2) Å],[31] bis(catechol)diborane−lutidine [B−O 1.489(2), 1.498(2) Å][32] as well as in the bis(catechol)borate anion [B−O 1.470−1.485(9) Å].[30] Also, the B−N bonds are shorter in **6** than in catecholborane−oxazolidine [1.541(2) and 1.548(2) Å] or the lutidine adduct [1.659(2) Å]. The structural parameters of **6**, therefore, show the inductive effect of the isothiocanate group.

Compound **8** has an unusual and unexpected structure. It is one of the rare examples of a complexed sodium sodiate. The cation, [Na(18-crown-6)(thp)$_2$]$^+$, is rather similar to [Na(18-crown-6)(THF)$_2$]$^+$. Obviously, the anion [(9-BBN)NCS]$^-$ is a fairly good base as it coordinates twice to a sodium ion through Na−S bonds. Its coordination sphere is completed by the addition of four thp molecules. A relationship with the so-called "ate complexes" is noticeable.

It follows from the present study that the NCS$^-$ ion coordinates to boron centers through its N atoms favoring (isothiocyanato)borate structures. The study of substituted hydroborates offers interesting insights into the coordination chemistry of their alkali metal salts. It seems that small effects of the ligands determine their structure. So, neither the sulfur atom nor the BH_3 hydrogen atoms of H_3B-NCS^- are able to replace a THF molecule from [Na(18-crown-6)(THF)$_2$]$^+$ in contrast to the sulfur atom of (9-BBN)NCS$^-$ in the presence of tetrahydropyran.

Experimental Section

General: All experiments were conducted under anhydrous conditions (N_2 blanket or vacuum). Commercial grade chemicals were used, and solvents dried by conventional procedures. NMR spectroscopic data were recorded with a Jeol 400 instrument, and IR data were taken with a Nicolet FT 20 instrument. Raman spectra were recorded with a Perkin−Elmer 2000 NIR FT spectrometer operated with an Nd-YAG laser at 1064 nm. For X-ray structure determinations a Siemens P4 diffractometer equipped with a CCD detector and an LT 2 low-temperature device and Mo-K_α radiation was used. Microchemical analyses were performed at the departmental microanalytical laboratory.

Crown Ether Complexes of Na(NCS): Na(SCN) was dissolved in THF and an equimolar amount of the crown ether (18-crown-6, 15-crown-5) added. After partial removal of the solvent, the solution was kept in the refrigerator. The crystals which formed within a few days were isolated and used for X-ray structure determination. The yield was not determined and no analysis performed.

Sodium Trihydro(isothiocyanato)borates. a) A solution of BH_3 in THF (2.12 mmol, 50 mL) was added with vigorous stirring to a suspension of Na(NCS) (0.508 g, 6.27 mmol) in THF (50 mL). The suspension turned rapidly into a clear solution. ^{11}B NMR spectroscopy showed that more than 90% of the borane had been consumed. Then, a solution of 18-crown-6 (1.925 g, 7.28 mmol) in 10 mL of THF was added followed by the addition of methylcyclohexane. This produced a white precipitate which was isolated by filtration and, after drying in vacuo, was found to have the composition Na(18-crown-6)(H_3B−NCS). Yield: 1.7 g (74%). From the filtrate, which was kept at 8 °C, a few single crystals of [Na(18-crown-6)$(THF)_2$][H_3B−NCS] (**1**) separated after several days; m.p. 155 °C (dec.). $C_{13}H_{27}BNNaO_6S$ (359.15): calcd. C 43.37, H 7.58, N 3.90, S 8.92; found C 43.28, H 7.48, N 3.77, S 8.93. ^{11}B NMR (THF): $\delta = -27.3$ (q, $^1J_{^1H^{11}B} = 96$ Hz) ppm. ^{13}C NMR: $\delta = 128.4$ (t, $^1J_{^{13}C^{14}N} = 24$ Hz) ppm. ^{14}N NMR: $\delta = 128.4$ ($^1J_{^{11}B^{14}N} = 25$ Hz) ppm. IR: $\tilde{\nu} = 2365$ m, 2325 m, 2172 st, 1353 m, 1248 m, 1155 m, 1109 st, 969 st, 840 m cm^{-1}. Raman (crystals): $\tilde{\nu} = 2918$ st, 2833 st, 2361 w, 2331 w, 2150 m, 1477 m, 1281 m, 1264 m, 1244 m, 863 st cm^{-1}. **b)** The complex [Na(15-crown-5)][H_3B−NCS] (**2**) was prepared in a similar manner. No precipitate formed after addition of methylcyclohexane. Single crystals separated from the solution at 8 °C. These were isolated by filtration. X-ray structure determination showed them to be [Na(15-crown-5)THF]-[H_3B−NCS]. The compound was isolated from the filtrate after partial evaporation of the solvents. After drying in vacuo, it was found to have the composition Na(15-crown-5)(H_3B−NCS). Yield: 676 mg (85%); m.p. 168 °C (dec.). $C_{16}H_{34}BNNaO_5S$ (375.13): calcd. C 41.60, H 7.25, N 3.73, S 8.54; found C 41.80, H 6.92, N 3.72, S 8.28. IR: $\tilde{\nu} = 2365$ m, 2307 m, 2161 st, 1349 m, 1248 m, 1154 m, 1105 st, 963 st, 839 m cm^{-1}.

***B*-(Isothiocyanato)catecholborane:** Trimethylsilylisothiocyanate (2.0 mL, 1.80 g, 14.2 mmol) was added to a solution of *B*-bromocatecholborane (1.722 g, 8.699 mmol) in toluene (10 mL). After refluxing the solution for 24 h, the ^{11}B NMR spectrum showed a quantitative reaction. All volatile components were removed in vacuo (1 Torr). The residue (1.22 g of a brown oil) was heated to 100 °C in vacuo. From the gas phase a solid separated as a colorless powder which, on storing, turned slowly orange. The product quickly hydrolyzes in moist air. Yield: 1.16 g (75%); m.p. 146−148 °C (dec.). $C_7H_4BNO_2S$ (177.01): calcd. C 47.51, H 2.28, N 7.91, S 18.11; found C 48.89, H 2.63, N 7.97, S 17.31. ^1H NMR ($CDCl_3$): $\delta = 7.1-7.2$ (m) ppm. ^{11}B NMR: $\delta = 18.1$ ppm. ^{13}C NMR: $\delta = 112.8$ (C-2/5), 123.7 (C-3/4), 147.4 (C-1/6), 143.1 (br., NCS) ppm. ^{14}N NMR: $\delta = -280$ ppm. IR: $\tilde{\nu} = 2074$ m, 1625 m, 1473 st, 1440 st, 1351 st, 1349 st, 1096 st, 808 st, 741 w cm^{-1}. Raman: $\tilde{\nu} = 3071$ m, 2092 w, 1627 m, 1440 m, 1399 st, 1231 st, 1142 w, 1006 m, 810 m, 612 w cm^{-1}.

Sodium Catecholatobis(isothiocyanato)borate (6): A solution of Na(NCS) (0.194 g, 2.39 mmol) in THF (10 mL) was added with stirring to a solution of *B*-(isothiocyanato)catecholborane (0.429 g, 2.42 mmol) in THF (5 mL). Stirring was continued at 0 °C for 1 h, then 18-crown-6 (0.91 g, 3.4 mmol) was added. After addition of methylcyclohexane (10 mL), the clear solution turned turbid. Insoluble material was removed by filtration and the filtrate kept at −20 °C. Within 1 d [Na(18-crown-6)$(THF)_2$][catB$(NCS)_2$] separated as colorless prisms (used for X-ray structure determination) which, on drying in vacuo, lost THF and became opaque. Yield 1.04 g of [Na(18-crown-6)][catB$(NCS)_2$] (65%); m.p. 51−54 °C. $C_{20}H_{28}BN_2NaO_8S_2$ (522.13): calcd. C 45.99, H 5.40, N 5.36, S. 12.27; found C 46.88, H 5.64, N 4.76, S 11.80. ^1H NMR ([D_8]THF): $\delta = 6.4-5.5$ (m) ppm. ^{11}B NMR: $\delta = -0.1$ (quint, $^1J_{^{11}B^{14}N} = 24$ Hz) ppm. ^{13}C NMR: $\delta = 108.7$ (C-2/5), 118.5 (C-3/4), 151.1 (C-1/6), 130.9 (br., NCS) ppm. ^{14}N NMR: $\delta = -248$ (1:2:3:2:1 quint, $^1J_{^{13}C^{14}N} = 24$ Hz) ppm.

Sodium (Isothiocyanato)-9-boratabicyclo[3.3.1]nonane: A solution of Na(NCS) (0.530 g, 6.54 mmol) in THF (35 mL) was added at 0 °C with stirring to a solution of 9-BBN (0.803 g, 6.59 mmol) in THF (15 mL). After warming to ambient temperature, 18-crown-6 was added (2.00 g, 7.57 mmol) followed, after some time, by methylcyclohexane (10 mL). A precipitate formed which was isolated by filtration. After drying in vacuo, the product was practically free of THF. Cooling the filtrate to −20 °C afforded small amounts of clear needles which were highly intergrown. They were used for X-ray crystal structure determination. NMR spectroscopic data were obtained from a freshly prepared solution in THF (without adding the crown ether). Single crystals suitable for an X-ray structure determination were obtained by recrystallization of the crystals from tetrahydropyran. Yield (from THF): 2.84 g (71%); m.p. 98−102 °C (dec.). $C_{21}H_{39}BNNaO_6S$ (467.25): calcd. C 53.96, H 8.41, N 3.00, S 6.86; found C 49.88, H 8.21, N 2.97, S 6.75. ^{11}B NMR (THF): $\delta = -11.4$ (d, $^1J_{^{11}B^1H} = 100$ Hz) ppm. ^{13}C NMR: $\delta = 26.1$, 26.3 ($CH_2\mathit{CH_2}CH_2$), 31.2, 34.5 ($CH\mathit{CH_2}CH_2$), 125.8 (NCS) ppm. ^{14}N NMR: $\delta = -224$ ($h_{1/2} = 75$ Hz) ppm. IR (nujol): $\tilde{\nu} = 2301$, 2271 w, 2231 w, 2138 st, 2069 st, BH, 1472 m, 1352 st, 1248 m, 1112 st, 1058 m, 967 st, 671 m cm^{-1}.

X-ray Structure Determinations: Suitable crystals were selected from the solution, in most cases at −20 °C, and covered with perfluoro ether oil. The selected crystal was mounted on a glass fiber and put rapidly on the goniometer head which was flushed with cold nitrogen gas. The size of the unit cell was determined from the data of five sets of 15 frames taken at different orientations, using the program SMART.[33] Data collection was performed with the program SMART[33] and data from 1250 frames were used for data reduction (program SAINT[33]). Structure solutions were performed by direct methods in SHELX 97.[34] Non-hydrogen atoms were refined anisotropically, hydrogen positions on C atoms were in most cases observed, but were put in calculated positions. The BH hydrogen atoms were found in the Fourier map and were freely refined using isotropic thermal parameters. Table 7 shows relevant crystallographic parameters and data related to structure solution and refinement. In Figures 1−7 the thermal ellipsoids are depicted at a 25% probability level. CCDC-217263 to -217269 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retriev-

Table 7. Crystallographic data and data related to structure solution

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**8**
Empirical formula	$C_{21}H_{43}BNNaO_8S$	$C_{15}H_1BNNaO6S$	$C_{17}H_{32}BNNaO_7S$	$C_{11}H_{20}NNaO_5S$	$C_{47}H_{45}N_{11}Na_2S_2$	$C_{28}H_{44}BN_2NaO_{10}S_2$	$C_{60}H_{11}B_2N_2Na_2O_{12}S_2$
Formula mass	503.42	387.27	417.49	301.33	437.02	666.57	1184.23
Crystal size [mm]	0.30 × 0.30 × 0.30	0.20 × 0.30 × 0.20	0.20 × 0.20 × 0.20	0.50 × 0.10 × 0.01	0.40 × 0.40 × 0.30	0.50 × 0.20 × 0.20	0.30 × 0.20 × 0.1
Crystal system	triclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$Pmn2_1$	$I2/a$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.1572(8)	10.2715(9)	8.079(7)	12.087(1)	14.232(5)	9.3035(6)	11.793(2)
b [Å]	9.2664(8)	13.391(1)	16.947(2)	7.2845(9)	9.506(4)	13.472(1)	16.438(4)
c [Å]	9.3535(8)	15.754(1)	16.557(2)	8.343(1)	36.29(2)	14.672(1)	19.069(4)
α [°]	89.667(2)	90	90	90	90	78.2700(1)	67.538(4)
β [°]	86.394(2)	90	100.869(2)	90	99.156(9)	87.6120(1)	82.468(5)
γ [°]	62.840(1)	90	90	90	90	75.1770(1)	85.903(4)
V [Å^3]	704.5(1)	2166.9(3)	2226.2(3)	734.6(2)	4847(4)	1740.4(2)	3386(1)
Z	1	4	4	2	4	2	2
ρ(calcd.) [Mg/m^3]	1.187	1.187	1.246	1.362	1.198	1.272	1.162
μ [mm^{-1}]	0.171	0.196	0.200	0.264	0.172	0.218	0.148
F(000)	272	832	896	320	1832	708	1290
Index range	$-11 \le h \le 11$ $-11 \le k \le 11$ $-11 \le l \le 11$	$-11 \le h \le 11$ $-14 \le k \le 14$ $-17 \le l \le 17$	$-8 \le h \le 8$ $-21 \le k \le 20$ $-20 \le l \le 21$	$-15 \le h \le 11$ $-9 \le k \le 9$ $-10 \le l \le 10$	$-16 \le h \le 11$ $-12 \le k \le 12$ $-46 \le l \le 46$	$-12 \le h \le 9$ $-16 \le k \le 16$ $-18 \le l \le 18$	$-14 \le h \le 16$ $-21 \le k \le 21$ $-22 \le l \le 23$
2θ [°]	58.18	46.52	55.68	56.48	58.72	58.38	38.46
Temp. [K]	183(2)	193(2)	193(2)	193(2)	193(2)	193(2)	193(2)
Refl. collected	4157	9645	12313	4159	13877	10172	19970
Refl. unique	2170	3115	3416	1554	4792	5338	10513
Refl. observed (4σ)	1780	2655	2408	1293	2354	3588	4444
R (int.)	0.0164	0.0557	0.0458	0.0384	0.0515	0.0236	0.0443
No. variables	218	227	244	194	281	397	766
Wt. scheme	0.0674/0.2171	0.1083/0.8019	0.0795/0.3187	0.058/0.00	0.0585/0.00	0.0803/0.6382	0.1413/0.00
GOOF	1.054	1.029	1.025	1.035	0.892	1.071	0.900
Final R. (4σ)	0.0472	0.595	0.0500	0.0549	0.0439	0.0538	0.075
Final $wR2$[a]	0.1288	0.1639	0.1290	0.1170	0.938	0.1482	0.1930
Largest res. peak	0.237	0.493	0.206	0.419	0.258	0.442	0.504

[a] $w^{-1} = s^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

ing.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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