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Crystal and Molecular Structure of Ammonia-Isothiocyanoborane, $NH_3 \cdot BH_2NCS$

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The crystal and molecular structure of $NH_3 \cdot BH_2NCS$, ammonia-isothiocyanoborane, has been determined. Distances from boron to nitrogen are 1.534 (8) Å to the NCS group and 1.578 (8) Å to the NH_3 unit. Unit cell distances are $a = 9.250$ (1), $b = 6.781$ (1), and $c = 7.152$ (1) Å. The space group is *Pnma*, and there are four molecules in the unit cell. Full-matrix least-squares refinement has yielded a value of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.043$ for 324 X-ray diffraction maxima measured on a Picker four-circle diffractometer. Comments are given on the relationship of this compound to other isothiocyanoboranes.

Reaction of B_2H_6 as an electrophile toward NH_4SCN has been reported to give NH_4^+,BH_3SCN^-, which loses H_2 at 0–25° to yield $H_3N \cdot BH_2SCN$. We have undertaken an X-ray diffraction study of this last compound, which is an isothiocyanate, $H_3N \cdot BH_2NCS$, as described below.

The evidence that most, if not all, known compounds of large and small boranes with thiocyanate are isothiocyanates is primarily spectroscopic. The correct structure for 6-$B_{10}H_{13}NCS$ was inferred from infrared and nmr spectra, but the conclusions left unresolved the possibility that the NCS ligand was in a bridge position. We show in the preceding paper[1] that the NCS is bonded through N to the B(6) atom. Most of the NCS compounds of boron prepared and examined by Lappert and Pyszora[2] showed NCS asymmetric stretching frequencies in a narrow range and were formulated as isothiocyanates. Although 6-$B_{10}H_{13}NCS$[1,3] and $(t\text{-BuNBNCS})_4$,[4] known to be isothiocyanates, also absorb in this range, neither $H_3N \cdot BH_2NCS$ nor BH_3NCS^- (as the dioxanate) conforms to the expected pattern. We therefore felt that an X-ray diffraction study was desirable.

Experimental Section

Preparation. The compound $H_3N \cdot BH_2NCS$ was prepared by adding diborane to ammonium thiocyanate in dimethoxyethane.[5] The diborane was generated by slow addition of $NaBH_4$ in 2-methoxyethyl ether (diglyme) to boron trifluoride etherate also in diglyme.[6] A stream of dry nitrogen carried the 0.083 mol of diborane (assuming 100% yield) into a flask containing 0.04 mol of ammonium thiocyanate in dimethoxyethane. After hydrogen evolution ceased, the glyme was removed, leaving an oil which crystallized at 4°. Crystals were dissolved in ethyl ether, petroleum ether was added, and high-quality crystals appeared within 1 hr.

X-Ray Data. Needles mounted with the elongated *b* axis along the goniometer axis were photographed by Weissenberg (*h0l, h1l*) and precession (*0kl, 1kl, hk0, hkl*) methods. Laue symmetry D_{2h}-*mmm* and extinctions consistent with either space group *Pnma* or $Pn2_1a$ were found. The unit cell dimensions, $a = 9.250$ (1), $b = 6.781$ (1), and $c = 7.152$ (1) Å, were established by a least-squares fit of Bragg angles of 27 reflections, carefully measured on a Picker diffractometer. We determined a crystal density of 1.30 g/cm³ by flotation in bromobenzene–xylene. This value is in reasonable agreement with the density of 1.31 g/cm³ calculated on the assumption that there are four molecules per unit cell.

Three-dimensional X-ray data were collected from a crystal about 0.16 mm × 0.16 mm × 0.28 mm (along *b*) on a four-circle Picker automatic diffractometer. Using Cu Kα radiation filtered through Ni foil, reflections were scanned through ω over an interval of 3.2° at 1°/min. Background counts were taken before and after each scan, holding the crystal stationary. Both incident and diffracted beam collimators were 0.5 mm in diameter.

Two asymmetric units of data were collected, and the data were then corrected for absorption ($\mu = 46.4$ cm^{-1}). Transmission coefficients ranging from 0.440 to 0.562 were calculated by a gaussian quadrature method.[7] The favorable crystal shape allowed us to make equal corrections for symmetry-related reflections. Those symmetry-related reflections for which $I > 0.5\sigma(I)$ were averaged, yielding a value of

$$R' = \sum_{H,i} |I_{H,i} - \bar{I}_H| / \sum_{H,i} \bar{I}_H = 0.012$$

where H is *hkl*, $I_{H,i}$ is the intensity of reflection H in data set i, and $\bar{I}_H$ is the average value of reflection H. Of the 350 symmetry-distinct reflections having $2\theta < 118°$, those 324 having $I > 0.5\sigma(I)$ were included in the structure determination and refinement. Values of $\sigma(I)$ are given by $\sigma(I) = [C + (T_c/2T_b)^2(B_1 + B_2)]^{1/2}$, where C is the total count for the scan, B_1 and B_2 are the background counts, T_c is the scan time, and T_b is the time for a single background count.[8]

Solution of the Structure and Refinement. The major peaks of a Patterson map at $v = 0.0$ and 0.5 immediately indicated the space group *Pnma*, in which all nonhydrogen atoms must lie on a mirror plane. Phases calculated from the sulfur position yielded an electron density map showing all nonhydrogen atoms. At this stage the value of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ was 0.33. Refinement, eventually including anisotropic thermal parameters constrained by the mirror plane, reduced R to 0.07. A difference electron density map then showed symmetry-related hydrogens of the BH_2 group, which were refined isotropically to $R = 0.059$. A subsequent difference electron density map revealed the hydrogens of the NH_3 group.

Final full-matrix refinement of all coordinates, anisotropic temperature parameters for nonhydrogen atoms, isotropic temperature parameters for hydrogens on boron, and fixed (7.0 Å²) temperature parameters for hydrogens on nitrogen led to $R = 0.043$. The value of $R_w = [\Sigma w(k^2F_o^2 - F_c^2)^2/\Sigma w(kF_o)^4]^{1/2}$ is 0.095. In these refinements, we minimized $\Sigma w(k^2F_o^2 - F_c^2)^2$, where k is the scale factor, $w = 1/F_o^2$ for $F_o > 4.62$, and $w = 1/4.62F_o$ for $F_o < 4.62$.

A final difference electron density map from which all atoms were subtracted showed electron density up to only 0.15 e/Å³, between nonhydrogen atoms and at the sulfur atom. This crystal would be a good candidate for study of bonding density, but we are reluctant to make an analysis of bonds in our present electron density. For comparison, we computed a final electron density map from which nonhydrogen atoms had been subtracted, showing maxima of 1.00 e/Å³ for hydrogen on boron and of 0.25 and 0.55 e/Å³ for the two symmetry-unrelated hydrogens on nitrogen. Some evidence was noted for oscillation of hydrogen about the B–NH_3 bond. No evidence was found for a statistical average of a crystal structure distorted from *Pnma* to $Pn2_1a$. Atomic scattering factors for B, C, N, and S were taken from the "International Tables for X-Ray Crystallography." The scattering factor for H was especially prepared for covalent hydrogen for use in the CRYRM computing system,[9] which was used for all refinements and electron density maps.

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Table I. Coordinates and Thermal Parameters[a]

Atom	x	y^b	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{13}$
S	0.5668 (2)	0.25	0.2598 (2)	78 (1)	209 (3)	142 (3)	38 (5)
C	0.4387 (6)	0.25	0.4157 (7)	90 (6)	200 (14)	98 (9)	−39 (16)
N1	0.3504 (6)	0.25	0.5264 (7)	93 (6)	263 (14)	119 (9)	30 (14)
B	0.2365 (7)	0.25	0.6823 (9)	68 (7)	251 (18)	122 (12)	24 (17)
N2	0.3247 (5)	0.25	0.8713 (7)	85 (6)	317 (17)	135 (10)	−11 (17)

Atom	x	y	z	B, Å^2
H1	0.166 (3)	0.388 (5)	0.669 (4)	2.6 (8)
H2	0.274 (8)	0.25	0.992 (9)	7.0[c]
H3	0.391 (5)	0.354 (7)	0.879 (6)	7.0[c]

[a] Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hl\beta_{13})]$. β_{12} and β_{23} are zero for atoms on the mirror plane. [b] Atoms with $y = 0.25$ are constrained to this mirror plane. [c] Not refined.

Results and Discussion

Coordinates and thermal parameters are in Table I, bond distances are in Table II, and bond angles are in Table III. A comparison of observed and calculated structure factors is available.[10]

The molecular and crystal structure is shown, projected along the *b* axis, in Figure 1. The distance between the in-plane hydrogen of NH_3 and the nearest sulfur atom of a different molecule is 2.62 Å. The other hydrogens of NH_3 are 2.89 Å from sulfur atoms of molecules in adjacent crystallographic mirror planes. These distances should be decreased by perhaps 0.1 Å from these values, because of the systematic distortion associated with bonding density toward hydrogen.[11] Inasmuch as the sum of van der Waals radii for sulfur and hydrogen is about 3.05 Å,[12,13] it is likely that these covalent NH bonds form weak hydrogen bonds to sulfur.[14] Molecules within a mirror plane are thus linked along the *a* axis, while molecules in adjacent mirror planes are hydrogen bonded to neighbors related by a center of symmetry. Adjacent hydrogen-bonded chains of molecules in a given mirror plane are held together by normal van der Waals contacts. Examples include an S· · ·N distance of 3.3 Å and an S· · ·HB distance of 3.34 Å.

A "normal" bond distance of 1.58 ± 0.02 Å between four-coordinated nitrogen and four-coordinated boron shows some correlation between distance and relative strengths of donor and acceptor.[15] For example, in the series where trimethylamine is donor, bond distances from nitrogen to boron are 1.636 (4) Å for BF_3, 1.610 (6) Å for BCl_3, 1.603 (20) Å for BBr_3, and 1.584 (25) Å for BI_3.[16] We would expect our H_3N-B bond to be most comparable with that of 1.581 (3) Å in $H_3NB_3H_7$[17] and not far from the single bonds for bridge N [1.574 (9) Å] and for terminal N [1.581 (7) Å] in $C_2H_5NH_2B_8H_{11}NHC_2H_5$.[18] Indeed, the H_3N-B distance in $H_3N{\cdot}BH_2NCS$ is 1.578 (8) Å, suggesting that BH_2NCS is a good acceptor.

Table II. Bond Distances (Å) with Standard Deviations in Parentheses

S–C	1.627 (6)	B–N2	1.578 (8)	N–H2	0.98 (7)
C–N1	1.137 (8)	B–H1	1.15 (4)	N–H3	0.93 (5)
N1–B	1.534 (8)				

Table III. Bond Angles (deg) with Standard Deviations in Parentheses

S–C–N1	179.2 (5)	N2–B–H1	111 (3)	B–N2–H3	113 (4)
C–N1–B	177.5 (6)	H1–B–H1′[a]	110 (4)	H2–N2–H3	105 (6)
N1–B–N2	105.5 (4)	B–N2–H2	121 (4)	H3–N2–H3′[a]	98 (6)
N1–B–H1	109 (3)				

[a] Primed atoms are related to unprimed ones by the molecular mirror plane.

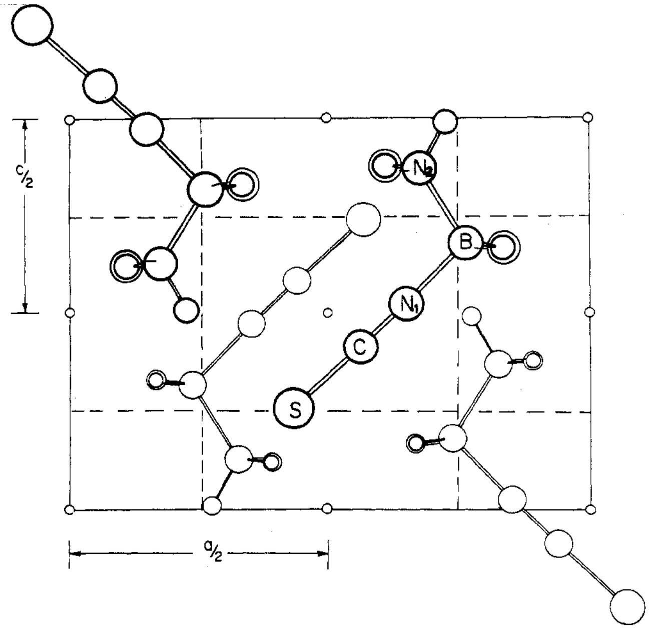

Figure 1. The crystal structure of $H_3N{\cdot}BH_2NCS$ in projection along the *b* axis. The darker two molecules are at $y = 0.75$; the lighter two are at $y = 0.25$.

As discussed in the preceding article, where the B–N distance in $B_{10}H_{13}NCS$ is only 1.43 Å, the possibility of conjugation can greatly reduce the bond length to an electron-deficient boron atom. However, the boron atom in $H_3N{\cdot}BH_2NCS$ is four-coordinated in a relatively simple fashion, so that the effect of the NCS group on its bond to B is much less: the distance is 1.534 (8) Å, comparable with that of 1.53 Å in the pyridine adduct to BF_3, $C_5H_5N{\cdot}BF_3$.[19] In resonance terms one might observe that conjugation is available for shortening the B–N bond in $B_{10}H_{13}NCS$, but only hyperconjugation is available for the bond from $H_3N{\cdot}BH_2$ to NCS in $H_3N{\cdot}BH_2NCS$.

The BNCS group is nearly linear in $H_3N{\cdot}BH_2NCS$, which has a B–N–C angle of 177.5 (6)° and an N–C–S angle of 179.2

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(5)°. This group tends toward linearity in $B_{10}H_{13}NCS$, where B(6)-N-C is 171.0 (6)° and N-C-S is 178.1 (6)°.[1] In contrast, methyl isothiocyanate is bent,[20] such that the CH_3-N-C angle is 142°. Starting from the neutral atom bond structure $H_3N{\cdot}H_2B{-}N{=}C{=}S$, we see that only the hyperconjugative $H_3N{\cdot}H_2{}^+B^-{=}N{=}C{=}S$ resonance forms shorten the B—N (to NCS) bond by multiple-bond resonance. We would expect the form $H_3NH_2B{-}N^+{\equiv}C{-}S^-$ to be of even greater importance than hyperconjugation in a linear BNCS structure, and we note that the shortened NC length of 1.137 (8) Å and the lengthened CS bond length of 1.627 (6) Å support a moderate contribution of this resonance form. Both resonance forms which involve charge separation are probably enhanced by hydrogen bonding in the crystalline solid.

Thiocyanate is an ambidentate ligand. It can bond through either the N or S atom.[21] The principal determinant of the binding mode is the acceptor atom, but many other factors can be important. For example, linkage isomerism is caused by solvent,[22] the influence of other ligands,[23] the counterion present,[24] and kinetic control.[25] Several explanations of donor-acceptor behavior have been advanced which offer at least qualitative rationalizations of the available data. Models with at least two parameters are needed to explain ambidentate behavior. Classification can be made in terms of basicity and polarizability, hard and soft,[26] class a or b acceptors,[27] or charge or frontier control.[28] In some examples quantitative results are possible.[29]

A review of the pseudohalides of group IIIb and IVb elements (excluding carbon) found that only isothiocyanates occur.[30] When NCS^- attacks carbon, both thiocyanates and isothiocyanates are produced. In most cases the isothiocyanate is thermally more stable and can be formed from the thiocyanate.[31] Preference for isothiocyanate formation increases in the order primary to secondary to tertiary carbon derivatives (often halides) and is favored by aryl, ethylenic, or carbonyl substituents.[32]

Lappert, *et al.*,[33] have studied three-coordinate mononuclear boranes and have prepared a "conversion series" in which compounds can be converted to ones further to the right as follows: $>BBr \rightarrow >BS^- \rightarrow >BCN \rightarrow >BCl \rightarrow >BNCS \rightarrow >BNCO \rightarrow >BO^-$. The observed preference for nitrogen over sulfur by boron (the NCS compounds are undoubtedly isothiocyanates, see later) is also shown in ligand displacement reactions of $B_{10}H_{12}L_2$.[34] Ligands are ranked in order of increasing bonding strength as follows: $Me_2S < MeCN < Et_2NCN < HCONMe_2 = AcNMe_2 < Et_3N = C_5H_5N = PhP$.

Lappert and Pyszora have prepared and examined a number of boron isothiocyanates[35,36] and have concluded that they do indeed have the iso structure. A principal line of evidence is infrared spectra. The NCS asymmetric stretching vibration occurs at a frequency of 2089 ± 31 cm^{-1} in a number of compounds.[37] For alkyl and aryl isothiocyanates the asymmetric stretching vibration occurs in the region 2045-2106 cm^{-1}, while for similar thiocyanates it is in the range 2137-2174 cm^{-1}.[38] Two known isothiocyanates, $(t\text{-}BuNBNCS)_4$ and $B_{10}H_{13}NCS$, absorb at 2078 and 2080 cm^{-1}, respectively. The band is at 2090 cm^{-1} in $Et_3N{\cdot}B(NCS)_3$.[39] However, the asymmetric stretch is a doublet at 2160 and 2050 cm^{-1} in $H_3N{\cdot}BH_2NCS$ and is quite similar in the dioxanate of $NaBH_3NCS$, occurring[1] at 2175 and 2085 cm^{-1}. Thus it would seem that the BH_3NCS^- salts, originally given as BH_3SCN^- salts,[5] are isothiocyanates as are the compounds of Lappert and Pyszora, although the asymmetric stretching frequency may not be an infallible guide.

The formations of (1) $H_3N{\cdot}BH_2NCS$ from NH_4NCS and $R_2O{\cdot}BH_3$, (2) $B_{10}H_{13}NCS$ from Hg $(NCS)_2$ and $B_{10}H_{12}(Me_2S)_2$ or from NaSCN and $B_{10}H_{14}$ (by way of $B_{10}H_{12}NCS^-$), and (3) $(t\text{-}BuNBNCS)_4$ from KSCN and $(t\text{-}BuNBCl)_4$ suggest that, when thiocyanate ion acts as a nucleophile toward boron, isothiocyanates are produced. The many examples of halogen replacement by the NCS^- ion are, as previously suggested, also isothiocyanates.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2920.

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