Isolation, Characterization, and Molecular Structure of 1,2-$(Me_2S)_2B_{12}H_{10}$

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Introduction

Although charge-compensated complexes of general formula $L_2B_{12}H_{10}$ have been synthesized with a number of ligands (e.g., L = CO,[1,2] R_3N,[3−5] R_3P,[6] R_2S[6−11]), many papers on this subject do not address the issue of the possible existence of isomers of these compounds. In those rare cases where the isolation of the individual isomers was reported,[2,3,6,11] they were usually the 1,7 and 1,12 isomers regardless of L or the method of $L_2B_{12}H_{10}$ synthesis. The absence of a 1,2 isomer in isomeric mixtures was usually explained on steric grounds or not discussed at all. The only example of a 1,2-$L_2B_{12}H_{10}$ compound reported in the literature is 1,2-$(Me_3N)_2B_{12}H_{10}$ for which no NMR or X-ray data are available.[3] Here we report the first isolation of 1,2-$(Me_2S)_2B_{12}H_{10}$, its characterization and molecular structure, and some trends observed upon the comparison of properties of the three $(Me_2S)_2B_{12}H_{10}$ isomers.

Experimental Section

General Data. The $BH_3{\cdot}SMe_2$ complex with 5−10% excess dimethyl sulfide (Aldrich Chemical Co.) was used as received. Chromatography was performed on Selecto silica gel (230−400 mesh) (Fisher Scientific). ^{11}B and ^{1}H NMR spectra were obtained on a Bruker DRX-500 spectrometer at 160.5 and 500.1 MHz, respectively. Boron spectra were referenced externally to $BF_3{\cdot}OEt_2$ in C_6D_6. ^{13}C NMR spectra were obtained on a Bruker AC-300 spectrometer operating at 75.5 MHz. The infrared spectrum was recorded on a Mattson Polaris FTIR spectrometer.

Isolation of 1,2-$(Me_2S)_2B_{12}H_{10}$. The synthesis of 1,7- and 1,12-$(Me_2S)_2B_{12}H_{10}$ by the pyrolysis of $BH_3{\cdot}SMe_2$ was reported earlier.[11] In an attempt to scale-up the reaction the Parr bomb was charged with 50 mL of $BH_3{\cdot}SMe_2$ complex in air, cooled to −78 °C, evacuated, heated to 130 °C, and held at this temperature for about 12−13 h. The pressure inside the reactor was about 1000 psi. The volatiles were pumped away through a cold trap immersed in liquid nitrogen and the solid residue extracted with 250 mL of CH_2Cl_2. The insoluble material was mostly $[Me_3S][(Me_2S)B_{12}H_{11}]$[11] contaminated with some boric acid and $B_{12}H_{12}^{2-}$. About 50 mL of 1 M HCl was added to the dichloromethane solution, and the mixture was stirred vigorously to speed up the decomposition of products unstable with respect to acidic conditions and air (2−3 h). The organic layer was washed with water and dried with $MgSO_4$. After solvent removal, the residual solid was chromatographed on silica gel using a CH_2Cl_2−toluene mixture (2:3) as eluent. After all 1,12-$(Me_2S)_2B_{12}H_{10}$ had passed the column, the eluent was switched to pure CH_2Cl_2. ^{11}B and ^{1}H NMR spectra of 1,7-$(Me_2S)_2B_{12}H_{10}$ from the eluate indicated the presence of an impurity, another boron compound. The latter could not be removed by simple recrystallization of the 1,7 isomer from toluene. However, 0.145 g of it was isolated by column chromatography on silica gel using a dichloromethane−toluene mixture (4:1) as eluent. It was identified as 1,2-$(Me_2S)_2B_{12}H_{10}$ (1.3% yield). Pure material for characterization was obtained after recrystallization from CH_2Cl_2−hexane.

Table 1. Crystallographic Data for 1,2-$(Me_2S)_2B_{12}H_{10}$

empirical formula	$C_4H_{22}B_{12}S_2$	vol, Å^3	6180.4(6)
formula weight	264.08	Z^a	4
crystal system	monoclinic	ρ_{calcd}, g cm^{-3}	1.135
space group	$P2_1/a$	T, °C	−60
a, Å	22.484(1)	radiation (λ, Å)	Mo Kα (0.710 73)
b, Å	13.004(1)	μ, mm^{-1}	0.311
c, Å	22.456(1)	$R_1{}^b$ [$I > 2\sigma(I)$]	0.056
β, deg	109.73(1)	w$R_2{}^c$ (all data)	0.146

[a] The total number of 1,2-$(Me_2S)_2B_{12}H_{10}$ molecules in the unit cell is 16; 4 of them are independent molecules. [b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Spectroscopic Data. $^{1}H\{^{11}B\}$ NMR (CD_3CN): δ 2.58 (s, 6H, $S(CH_3)_2$), 1.55 (br s, 4H, H4, H5, H7, H11), 1.46 (br s, 4H, H3, H6, H9, H12), 1.40 (br s, 2H, H8, H10). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ 26.2 (s, $S(CH_3)_2$). ^{11}B NMR (CD_3CN): δ −10.5 (s, B(1,2)), −13.9 (d, J_{B-H} = 105 Hz, B(9,12)), −14.3 (d, J_{B-H} = 106 Hz, B(8,10)), −15.9 (d, J_{B-H} = 138 Hz, B(4,5,7,11)), −17.4 (d, J_{B-H} = 147 Hz, B(3,6)). IR (KBr): 3021 (s), 2930 (m), 2518 (vs), 1421 (s), 1408 (s),1336 (w), 1055 (m), 1029 (m), 1003 (m), 964 (s), 859 (m), 833 (m), 794 (w), 729 (m), 670 (w) cm^{-1}. MS (EI): calcd for $C_4H_{22}B_{12}S_2$, m/z = 264.084; obsd, m/z = 263.228.

X-ray Crystal Structure Determination. Crystals of 1,2-$(Me_2S)_2B_{12}H_{10}$ were grown by slow evaporation of solvents from an ethanol−acetonitrile−water solution. A crystal was mounted on the tip of a glass fiber. The crystallographic data were collected on an Enraf-Nonius Kappa CCD diffraction system with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using DENZO.[12]

The structure was solved by direct methods and refined using SHELXTL (difference electron density calculations, full least-squares refinements).[13] Crystals of 1,2-$(Me_2S)_2B_{12}H_{10}$ are twinned crystals. The final R_1 and wR_2 were 0.056 and 0.146, respectively, after the refinement. In contrast, the R_1 and wR_2 were 0.202 and 0.558, respectively, when the structure was refined without TWIN and BASF commands. The final refinement indicates that the ratio for the twin is 0.72:0.28. All non-hydrogen atoms were refined anisotropically. Table 1 gives crystallographic data, and Table 2 gives selected bond lengths and angles.

Results and Discussion

Since the dipole moment of $(Me_2S)_2B_{12}H_{10}$ will increase as the substituents on the cage move closer to each other, the most

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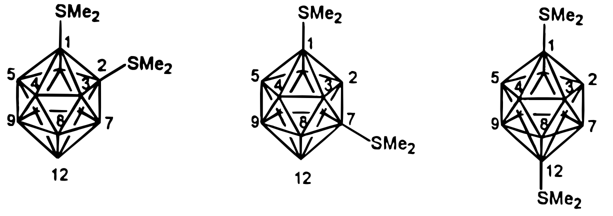
Table 2. Selected Bond Distances (Å) and Angles (deg) for 1,2-$(Me_2S)_2B_{12}H_{10}$

C1−S11	1.796(3)	B14−B19	1.769(6)
C2−S11	1.794(3)	B14−B18	1.771(6)
C3−S12	1.785(4)	B14−B15	1.803(5)
C4−S12	1.808(4)	B15−B110	1.779(6)
S11−B11	1.906(4)	B15−B19	1.781(6)
S12−B12	1.905(4)	B15−B16	1.792(5)
B11−B14	1.753(5)	B16−B110	1.778(6)
B11−B15	1.754(5)	B16−B111	1.789(6)
B11−B12	1.770(5)	B17−B112	1.788(6)
B11−B13	1.777(5)	B17−B18	1.789(6)
B11−B16	1.777(5)	B17−B111	1.796(5)
B12−B111	1.749(5)	B18−B19	1.776(6)
B12−B17	1.755(5)	B18−B112	1.782(6)
B12−B16	1.768(5)	B19−B112	1.781(6)
B12−B13	1.780(5)	B19−B110	1.787(6)
B13−B18	1.787(6)	B110−B112	1.773(6)
B13−B17	1.795(5)	B110−B111	1.773(6)
B13−B14	1.800(5)	B111−B112	1.771(6)
C2−S11−C1	102.07(19)	B17−B12−S12	124.7(2)
C1−S11−B11	105.63(18)	B16−B12−S12	117.4(2)
C2−S11−B11	104.76(18)	B11−B12−S12	117.1(2)
B14−B11−S11	123.5(2)	B13−B12−S12	119.2(2)
B15−B11−S11	123.9(2)	B12−B11−B16	59.77(19)
B12−B11−S11	117.8(2)	B12−B11−B13	60.3(2)
B13−B11−S11	117.9(2)	B16−B12−B11	60.3(2)
B16−B11−S11	119.2(2)	B11−B12−B13	60.06(19)
C3−S12−C4	102.5(2)	B14−B11−B12	108.8(3)
C3−S12−B12	104.92(18)	B15−B11−B12	108.6(3)
C4−S12−B12	105.28(18)	B111−B12−B11	108.8(3)
B111−B12−S12	123.8(2)	B17−B12−B11	108.7(3)

Chart 1



polar isomer out of three pictured in Chart 1 is the 1,2 isomer and the least polar is the 1,12 isomer. This is confirmed by the order in which isomers are eluted from a silica gel column by a dichloromethane−toluene mixture (4:1). The R_f values decrease as we proceed from the 1,12 isomer (0.53) to the 1,2 isomer (0.17), with that for the 1,7 isomer in between (0.44). On the other hand, 1,2-$(Me_2S)_2B_{12}H_{10}$ has the lowest melting point out of the three isomers. It melts with apparent decomposition at 266 °C. For the 1,7 isomer the melting point is 274 °C, and the 1,12 isomer still does not melt at 300 °C. Similar trends were previously reported for isomers of $(Me_3N)_2B_{12}H_{10}$.[3]

The 1,2 isomer has the same point symmetry as the 1,7 isomer (C_{2v}). Therefore, the number of signals and their relative intensities are the same in the ^{11}B NMR spectra of these compounds. Only the positions of the peaks are different (Figure 1a,b). At 160.5 MHz all five peaks are resolved in the ^{11}B NMR spectrum of the 1,2 isomer while two peaks overlap for the 1,7 isomer. The obvious assignments are B(1,2) for the most downfield peak of intensity 2 and B(4,5,7,11) for the only signal of intensity 4. A $^{11}B-^{11}B\{^1H\}$ 2D COSY experiment assisted in the assignment of the remainder of the peaks (Figure 2). On the basis of these assignments, the following trends in the spectra of the three isomers are noted. The farthest downfield peak always belongs to two boron atoms bearing sulfide substituents. It shifts slightly upfield as the substituents come closer to each other. The next most downfield peak always belongs to boron atoms not connected to any borons bearing the sulfide substituents (B(9,12) and B(8,10) in the 1,2 isomer, and B(9,10) in the 1,7 isomer). The chemical shift of the boron atoms connected to only one boron bearing the sulfide substituent barely changes from isomer to isomer and is almost the same as for a boron atom in $B_{12}H_{12}^{2-}$.[14] The highest upfield peak is due to the boron atoms connected to both boron atoms bearing the sulfide substituents (B(3,6) for the 1,2 isomer and B(2,3) for the 1,7 isomer). Comparison of the ^1H NMR spectra of the three isomers reveals that the methyl signal shifts upfield as the sulfur substituents move away from each other. The assignment of the peaks of the proton atoms on borons in 1,2-$(Me_2S)_2B_{12}H_{10}$ is made from a $^1H-^{11}B\{^1H\}$ 2D spectrum (HETCOR). The

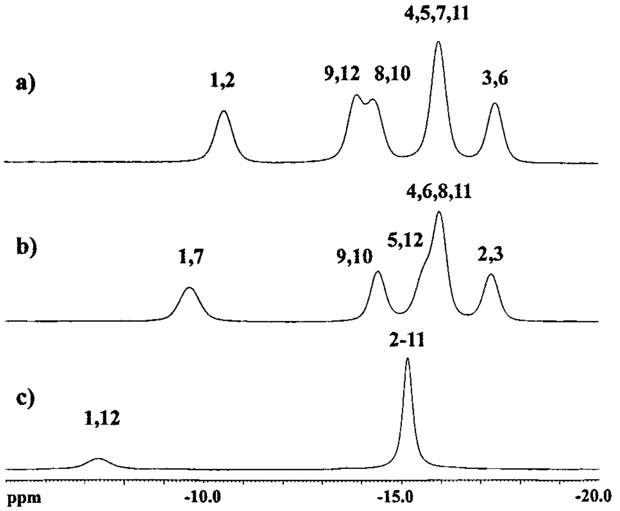


Figure 1. $^{11}B\{^1H\}$ NMR spectra of the 1,2 (a), 1,7 (b), and 1,12 (c) isomers of $(Me_2S)_2B_{12}H_{10}$ in CD_3CN.

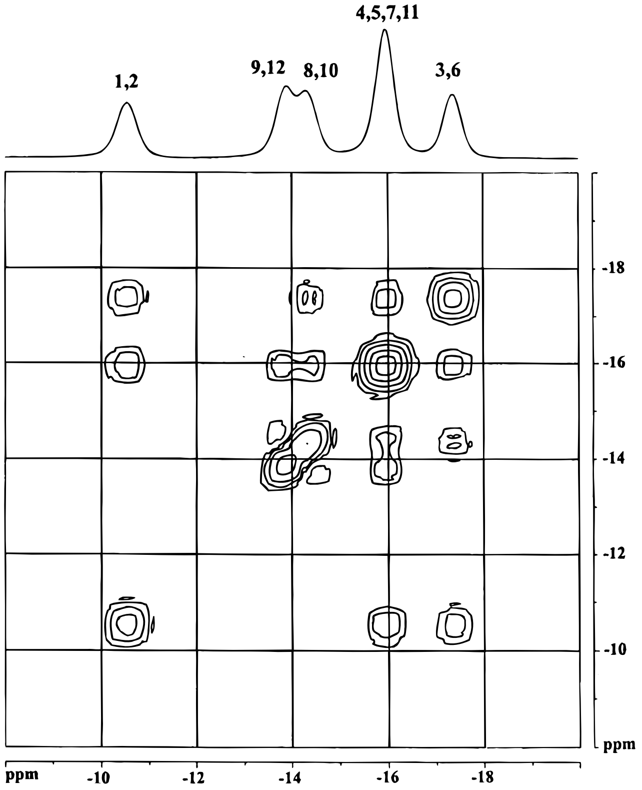


Figure 2. $^{11}B-^{11}B\{^1H\}$ 2D COSY spectrum of 1,2-$(Me_2S)_2B_{12}H_{10}$ in CD_3CN.

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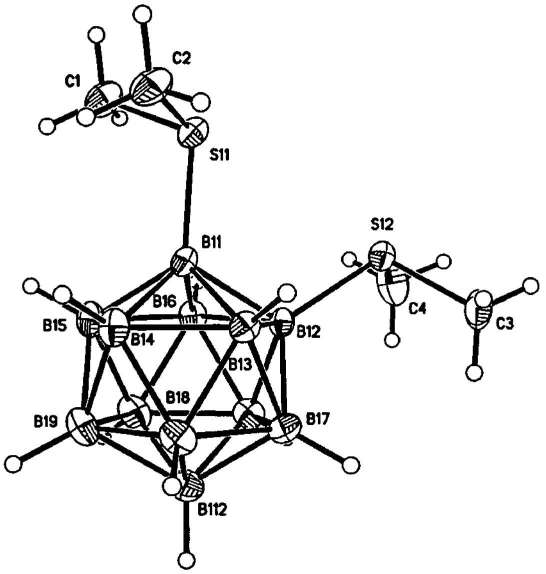

Figure 3. ORTEP plot of 1,2-$(Me_2S)_2B_{12}H_{10}$.

position of the methyl carbon signal in the ^{13}C NMR spectra of isomers is hardly influenced by the substitution pattern.

The NMR data obtained for 1,2-$(Me_2S)_2B_{12}H_{10}$ are in agreement with the molecular structure determined by X-ray single-crystal diffraction. 1,2-$(Me_2S)_2B_{12}H_{10}$ crystallizes in the monoclinic space group $P2_1/a$ with four crystallographically independent molecules. They all occupy general positions in the unit cell. Figure 3 displays one of the four 1,2-$(Me_2S)_2B_{12}H_{10}$ molecules. There is a *pseudo* mirror plane through borons 3, 6, 8, and 10 in all four molecules. The dimethyl sulfide ligands lie on opposite sides of this mirror plane with methyl groups pointed away from each other to reduce the steric interaction. The B−B bond lengths and B−B−B bond angles in these molecules range from 1.735(6) to 1.803(6) Å and from 58.8(2)° to 61.9(2)°, respectively. The B−S bond lengths are between 1.889(4) and 1.907(4) Å. The icosahedral boron framework in each molecule does not appear to be affected by SMe_2 substitution. Also, boron−sulfur bonds are tilted away from one of the boron−boron connectivities of an adjacent pentagonal face to reduce the steric interaction between methyl hydrogens and hydrogens on these boron atoms. For example, the angles B14−B11−S11 and B15−B11−S11 are 123.5° and 123.9°, respectively, whereas the other three angles at B11 containing the B11−S11 bond are less than 120° (Table 2, Figure 3). These results are consistent with those observed previously for the 1,7, and 1,12-$(Me_2S)_2B_{12}H_{10}$ and (Me_2S)-$B_{12}H_{11}$ monoanion.[11]

The low yield of the 1,2 isomer accounts for its not being detected previously[11] when the pyrolysis of $BH_3 \cdot SMe_2$ was run on an almost 1/10 scale compared with the present reaction. This isomer would be of great interest as it might serve as a precursor for the synthesis of bidentate chelating ligands and even thio crown ethers containing the icosahedral boron cage if yields can be improved. Studies toward the improved synthesis of 1,2-$(Me_2S)_2B_{12}H_{10}$ are currently underway.

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Supporting Information Available: Tables of crystallographic data, positional parameters, bond lengths and bond angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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