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Short Communications

Molecular Structure of Gaseous Tris(methylseleno)borane

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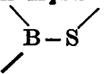
The tendency of boron to form partial double bonds with sulfur atoms seems now to be established both by experimental [1–4] and theoretical [7] methods. *Ab initio* calculations give a considerable barrier to rotation about the B – S bond in H_2BSH (about 20 kcal mol^{-1}) [7] and planar  arrangements have been found experimentally in a series of compounds. We have now extended these investigations to BSe compounds and report here the results of an electron-diffraction investigation of $B(SeCH_3)_3$.

The compound was synthesised by one of us (W.S.) and the electron-diffraction diagrams recorded with Balzers' eldigraph KD-G2 in Oslo.[8,9] The nozzle temperature was about 105 °C. Three sets of plates were obtained: Set 1 (4 plates, electron wavelength 0.05844 Å, nozzle-to-plate distance 578.82 mm), set 2 (5 plates, 0.05844 Å, 188.92 mm) and set 3 (4 plates, 0.05853 Å, 188.95 mm). Two average intensity curves were computed, one from the plates in set 1 covering the s-range 1.0 – 13.5 Å^{-1} and the other from the plates in set 2 and set 3 covering the s-range 3.25 – 40.0 Å^{-1}. The data were treated in the usual way [10] using the modification function $s/|f_B'||f_C'|$. The scattering amplitudes were calculated as described previously.[8]

The experimental radial distribution function (Fig. 1) calculated by Fourier inversion of a composite experimental intensity curve, showed that the heavy atom skeleton must be essentially planar and gave approximate values for the most important structural parameters. Least-squares refinements were then carried out assuming C_3 symmetry and no tilt of the methyl groups. The composite experimental intensity curve was used in some calculations, in others

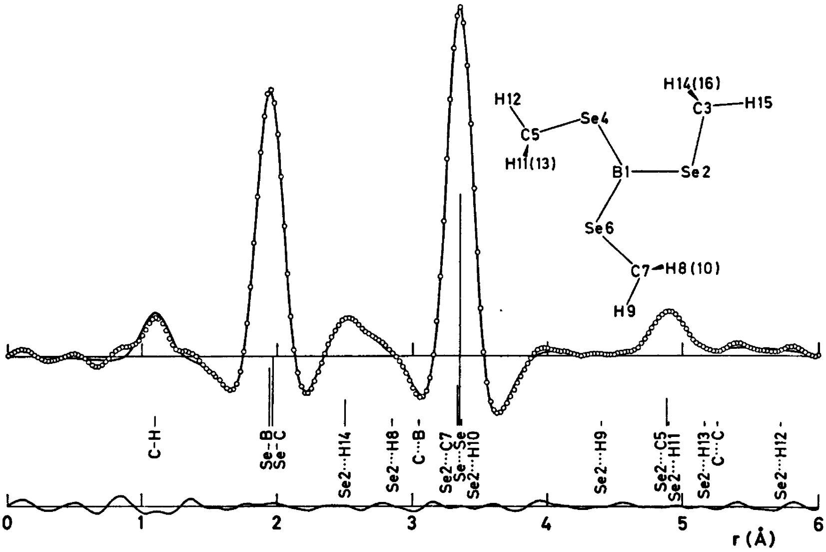


Fig. 1. Experimental (circles) and theoretical (full line) radial distribution functions for $B(SeMe)_3$ (artificial damping constant [10] $k = 0.002$ Å^2). The differences between experimental and theoretical values are also shown. The positions and approximate areas of the peaks corresponding to the most important interactomic distances are indicated.

Table 1. Bond distances, angles and mean amplitudes of vibration in tris(methylseleno)borane. The strandard deviations given in parentheses apply to the last digit given.

	r_a [16] (Å)	u (Å)		Angles (degrees)	
C – H[a]	1.102(15)	0.073(14)		∠SeCH	107.0(10)
Se – B[b]	1.936(2)	0.054	(5)	∠BSeC	102.5(5)
Se – C[b]	1.954(4)	0.051		ϕ(Se4B1Se2C3)[c]	2.0(171)
				ϕ(B1Se2C3H15)	165.0(65)

[a] All the C – H distances were assumed equal and an asymmetry constant $\varkappa = 0.00002$ Å^3 was used. [b] A shrinkage for the Se···Se distance equal to 0.003 Å was assumed;[4] if the shrinkage was neglected, 1.934 and 1.955 Å were obtained for the Se – B and Se – C distances. [c] See text for a discussion of the accuracy of this angle.

Table 2. The most important non-bonded distances and mean amplitudes of vibration.

	r_a (Å)	u (Å)		r_a (Å)	u (Å)	
Se···Se	3.350[a]	0.086(2)	Se2···H14	2.508	0.110(16)	
Se2···C5	4.890	0.107(9)	Se2···H8	2.876	0.300	b
Se2···C7	3.336	0.178(40)	Se2···H9	4.415	0.230	
C···C	5.253	0.213(50)	Se2···H10	3.330	0.300	
C···B	3.034	0.170[b]	Se2···H11	4.906	0.270	
			Se2···H12	5.731	0.200	
			Se2···H13	5.159	0.270	

[a] A shrinkage of 0.003 Å is included. [b] The value was not refined with the other parameters.

the two average intensity curves were used simultaneously without combining them. In the former case a diagonal weight matrix was assumed while in the latter a weight matrix with off-diagonal elements different from zero was used.[11] The data for $s > 33.25$ Å^{-1} were discarded in both cases.

Lack of the necessary spectroscopic information made it impossible to compute reliable mean amplitudes of vibration (u) and shrinkage effects from the force field. However, it seems likely that the values should be similar to those obtained for $B(SCH_3)_3$.[4] The results in Tables 1 and 2 are based on the values obtained in several least-squares refinements. Various weighting schemes were used, and various assumptions about the u-values which are difficult to refine, were tried. The results for the most important parameters, Se – B and Se – C bond lengths and ∠BSeC, were essentially the same in all the refinements. The standard deviations given include the effect of correlation between the intensity data as well as a 0.1 % uncertainty in the s-scale. The torsional angle, ϕ(Se4B1Se2C3), refines to a value close to zero, and the corresponding standard deviation becomes then unrealistically large. According to Hamilton's R-factor test [12] the torsional angle is less than 14° at the 99 % significance level. The planarity of the heavy atom skeleton is consistent with a non-negligible π-bond order in the $>B-Se<$ bonds.

Pauling gives 0.81 Å for the covalent radius of boron.[13] If the modified Schomaker-Stevenson rule,[13]

$$D(X-B) = r_X + r_B - 0.08|x_X - x_B| \quad (1)$$

is used, the pure single B – S and B – Se bond lengths are estimated to 1.81 and 1.95 Å, respectively. As opposed to other evidence, the comparison of these values with the observed bond lengths for $>B-S<$ (1.78 – 1.81 Å) and $>B-Se<$ (1.94 Å), seems to indicate no significant double bond character. However, the estimates of the pure single bond lengths are rather uncertain. If the observed B – C bond length in $B(CH_3)_3$ (1.58 Å [14]) is used, eqn. (1) gives $r_B = 0.85$ Å. This value is in agreement with the B – B bond length in B_2Cl_4 [1.702 (0.035) Å [15]]. The estimates of the pure single bonds become then $D(\mathrm{B-S}) = 1.85$ Å and $D(\mathrm{B-Se}) = 1.99$ Å, *i.e.* about 0.05 Å longer than the observed values in $\mathrm{B(SCH_3)_3}$ and $\mathrm{B(SeCH_3)_3}$ respectively. We conclude therefore that the π-bond order is non-negligible in $>\mathrm{B-Se}<$ as well as in $>\mathrm{B-S}<$ bonds.

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Density and Surface Tension of Molten Manganese—Cesium Chloride Mixtures

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Density and surface tension of molten $\mathrm{MnCl_2-CsCl}$ were investigated to supplement absorption [1] and Raman spectroscopic [2] studies. The density and surface tension were determined from liquidostatic weighing and the pin detachment force, respectively. The principle and experimental details have been previously described.[3–5]

Anhydrous salts were obtained from $\mathrm{MnCl_2 \cdot xH_2O}$ (*p.a.* Merck, Darmstadt, Germany) and

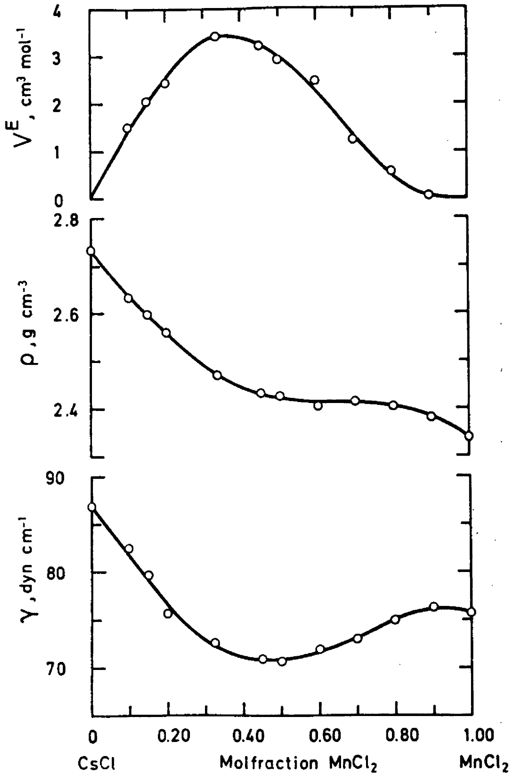

Fig. 1. Surface tension, γ; density, ϱ; and molar excess volume, V^E, for molten mixtures of CsCl and $\mathrm{MnCl_2}$ at 700 °C.

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