

Contribution from the Department of Chemistry, Colorado State University,  
Fort Collins, Colorado 80523**Crystal and Molecular Structure of 10,10'-[B<sub>10</sub>H<sub>8</sub>(S(CH<sub>3</sub>)<sub>2</sub>)]<sub>2</sub>, 10,10'-Bis(dimethyl sulfide)hexadecahydroicosaborane**OREN P. ANDERSON\*<sup>1</sup> and ANTHONY P. SCHMITT

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The crystal and molecular structure of 10,10'-[B<sub>10</sub>H<sub>8</sub>(S(CH<sub>3</sub>)<sub>2</sub>)]<sub>2</sub>, 10,10'-bis(dimethyl sulfide)hexadecahydroicosaborane, has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The light golden crystals are triclinic, space group *P*1̄ (No. 2), with one dimeric formula unit in a unit cell of dimensions  $a = 7.976$  (3) Å,  $b = 9.787$  (4) Å,  $c = 7.695$  (4) Å,  $\alpha = 92.04$  (1)°,  $\beta = 106.75$  (2)°, and  $\gamma = 111.90$  (1)°. The structure was refined by full-matrix least-squares methods to an  $R$  of 0.034 ( $R_w = 0.048$ ) for 1466 independent reflections with  $F^2 > 3\sigma(F^2)$ . The dimeric molecule exhibits crystallographically imposed  $\bar{1}$  symmetry relating the two B<sub>10</sub> units. The linkage between the B<sub>10</sub> units involves a pair of adjacent axial and equatorial boron atoms from each cage, forming two localized three-center B-B-B bonds (B2-B2' = 1.686 (4) Å, B1-B2' = 1.901 (3) Å). Each B<sub>10</sub> cage unit roughly possesses the configuration of a bicapped square antiprism, with the dimethyl sulfide moiety substituted at the remaining axial position (B<sub>10</sub>-S1 = 1.861 (2) Å). B-B distances within the B<sub>10</sub> unit range from 1.671 (3) to 1.969 (3) Å.

**Introduction**

Bridged boranes composed of *closo*-borane fragments are rare species,<sup>2</sup> with the only structurally characterized examples being the normal<sup>3</sup> and photo<sup>4</sup> isomers of B<sub>20</sub>H<sub>18</sub><sup>2-</sup>. On the basis of NMR<sup>5</sup> and x-ray structural work,<sup>3</sup> the linkage between the two B<sub>10</sub> cages in the normal isomer of the B<sub>20</sub>H<sub>18</sub><sup>2-</sup> ion has been characterized as involving a fused pair of closed, three-center B-B-B bonds, and recent theoretical work<sup>2</sup> has been in agreement with this interpretation.

A variety of substituted derivatives of the B<sub>20</sub>H<sub>18</sub><sup>2-</sup> ion of general formula B<sub>20</sub>H<sub>16</sub>L<sub>2</sub> are known.<sup>6,7</sup> The present study presents the crystal and molecular structure of 10,10'-bis(dimethyl sulfide)hexadecahydroicosaborane, 10,10'-[B<sub>10</sub>H<sub>8</sub>(S(CH<sub>3</sub>)<sub>2</sub>)]<sub>2</sub>. The structure of this neutral derivative of B<sub>20</sub>H<sub>18</sub><sup>2-</sup> has been determined in order to verify that the intercage linkage mode present in the normal isomer of B<sub>20</sub>H<sub>18</sub><sup>2-</sup> persists in this neutral derivative, to study the structural effect of the electron-withdrawing dimethyl sulfide group on the structure of the molecule, and to provide more precise structural parameters for this very interesting molecular unit. The precision in the results of the earlier crystallographic study<sup>3</sup> of the structure of the B<sub>20</sub>H<sub>18</sub><sup>2-</sup> ion was apparently strongly influenced by major disorder in the crystal, an effect which is not found in the crystals of 10,10'-[B<sub>10</sub>H<sub>8</sub>(S(CH<sub>3</sub>)<sub>2</sub>)]<sub>2</sub> studied here.

**Experimental Section**

The synthesis, crystallization, and characterization of the title compound have been previously described.<sup>7</sup> **Crystal Data.** For B<sub>20</sub>H<sub>28</sub>S<sub>2</sub>C<sub>4</sub> (mol wt 356.58), triclinic,  $a = 7.976$  (3) Å,  $b = 9.787$  (4) Å,  $c = 7.695$  (4) Å,  $\alpha = 92.04$  (1)°,  $\beta = 106.75$  (2)°,  $\gamma = 111.90$  (1)°,  $V = 526.7$  Å<sup>3</sup>,  $\rho_{\text{obsd}} = 1.12$  g cm<sup>-3</sup>,  $\rho_{\text{calcd}} = 1.12$  g cm<sup>-3</sup>,  $Z = 1$ ,  $F(000) = 184$ , space group *P*1̄, Mo K $\alpha$  radiation,  $\lambda_1$  0.709 30 Å,  $\lambda_2$  0.713 59 Å, and  $\mu(\text{Mo K}\alpha) = 2.3$  cm<sup>-1</sup>.

**Data Collection and Reduction.** Preliminary Weissenberg and precession photographs revealed only Laue symmetry  $\bar{1}$ , consistent with the space groups *P*1 and *P*1̄.<sup>8</sup> The centric space group *P*1̄ (No. 2) was chosen arbitrarily for all further structural work with this compound. The correctness of this choice is attested to only by the ultimate solution and refinement of this structure, as reported below.

The golden crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the  $c$  axis approximately coincident with the diffractometer  $\phi$  axis. The crystal was accurately centered, and the orientation matrix for data collection was obtained from least-squares calculations on the automatically determined<sup>9</sup>  $2\theta$ ,  $\chi$ , and  $\phi$  settings of 34 reflections with  $2\theta$  values in the range 16–24°. A least-squares calculation,<sup>10</sup> also based on the setting angles of these 34 reflections (determined at ambient temperature, 20 (±1) °C), provided the unit cell parameters reported above. The cell reported above is related to a conventional reduced cell of type II (negative

reduced form)<sup>11</sup> by the transformation matrix

$$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

The measured density reported was obtained by neutral buoyancy in aqueous ethanolic potassium iodide solution.

The intensities of 1848 unique reflections with  $5^\circ < \theta < 25^\circ$  were measured by  $\theta$ - $2\theta$  scans, employing Zr-filtered Mo K $\alpha$  radiation. The lower limit for  $\theta$  was purposely set at a high value to avoid possible low- $\theta$  cutoff of diffracted beams by the beam stop. The scan range was 1.0° to either side of the calculated K $\alpha$  peak position, at a constant scan rate of 10° min<sup>-1</sup>. The number of scans for a given reflection varied according to the intensity, with weak reflections scanned a maximum of four times. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and zirconium-foil attenuators were inserted automatically if the peak count rate exceeded 2500 counts s<sup>-1</sup>. The intensity of one of three reference reflections (300, 030, 003) was measured every 25 reflections. None of these control reflections showed any significant changes in intensity during the course of data collection.

Lorentz and polarization corrections were applied to the observed data. The uncertainty parameter,  $g$ , in the formula used for the standard deviation in the intensity<sup>12,13</sup> was taken as 0.03. Reflections with  $I > 3\sigma(I)$  were judged to be observed, and the 1466 reflections which met this criterion were employed in the solution and refinement of the structure. Due to the small absorption coefficient reported above and the small size of the data collection crystal (approximate dimensions 0.15 × 0.2 × 0.3 mm (long dimension along  $c$ )), no absorption correction was applied.

**Solution and Refinement of the Structure.** The position of one of the sulfur atoms was assigned from the highest nonorigin peak in the Patterson map. Since the unit cell contains only one unit of the dimer (see above), the dimer was required to possess the crystallographic  $\bar{1}$  symmetry, and the position of the second sulfur atom was generated by the center of symmetry at the special position (0, 1/2, 0). The positions of all nonhydrogen atoms were then obtained from a Fourier synthesis phased by the sulfur atom. Scattering factors for neutral sulfur, carbon, and boron were taken from ref 14. Scattering factors for spherically bonded hydrogen atoms<sup>15</sup> were also taken from ref 14, as were correction terms  $\Delta f''$  and  $\Delta f'''$  for anomalous dispersion due to sulfur.

Three cycles of full-matrix least-squares refinement (on  $F$ ) with all nonhydrogen atoms refined anisotropically lowered  $R$  ( $=\sum|F_o| - |F_c|/\sum|F_o|$ ) from its initial value of 0.34 to 0.07 (unobserved reflections not included) and  $R_w$  ( $=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ ) to 0.12. The NUCLS refinement program minimizes  $\sum w(|F_o| - |F_c|)^2$ , where  $F_o$  and  $F_c$  are the observed and calculated structure amplitudes, respectively, and  $w$  is the weight ( $=4F_o^2/\sigma^2(F_o^2)$ ). At this point a difference Fourier map clearly indicated the presence of the hydrogen atoms attached to the borane cage and the methyl carbon atoms (electron densities 0.3–0.5 e Å<sup>-3</sup>). In three final cycles of full-matrix

**Table I.** Atomic Coordinates (Fractional) and Isotropic Thermal Parameters<sup>a</sup>

Atom	x	y	z	B, Å <sup>2</sup>
S1	0.20479 (7)	0.12361 (5)	0.42596 (7)	
B1	-0.2134 (3)	0.3843 (2)	-0.0420 (3)	
B2	0.0217 (3)	0.4355 (2)	0.0619 (3)	
B3	-0.1439 (3)	0.3937 (2)	0.2014 (3)	
B4	-0.2841 (3)	0.2183 (2)	0.0452 (3)	
B5	-0.1256 (3)	0.2500 (3)	-0.0910 (3)	
B6	0.0979 (3)	0.2804 (2)	0.0762 (3)	
B7	0.0834 (3)	0.3871 (2)	0.2896 (3)	
B8	-0.1330 (3)	0.2265 (2)	0.2763 (3)	
B9	-0.1209 (3)	0.1262 (2)	0.0708 (3)	
B10	0.0667 (3)	0.2107 (2)	0.2651 (3)	
C1	0.2516 (4)	0.2203 (3)	0.6476 (3)	
C2	0.4352 (4)	0.1927 (5)	0.3998 (5)	
H1	-0.334 (3)	0.400 (2)	-0.137 (3)	3.2 (4)
H3	-0.181 (3)	0.471 (2)	0.277 (3)	3.6 (4)
H4	-0.435 (3)	0.153 (2)	0.002 (3)	3.9 (5)
H5	-0.147 (3)	0.213 (2)	-0.228 (3)	3.9 (5)
H6	0.216 (3)	0.293 (2)	0.037 (3)	2.8 (4)
H7	0.204 (3)	0.474 (2)	0.404 (3)	4.0 (5)
H8	-0.198 (3)	0.184 (2)	0.381 (3)	3.3 (4)
H9	-0.171 (3)	0.004 (2)	0.025 (3)	3.4 (4)
H11	0.134 (5)	0.202 (3)	0.665 (4)	6.2 (7)
H12	0.330 (4)	0.185 (3)	0.731 (4)	6.9 (7)
H13	0.320 (4)	0.322 (3)	0.655 (3)	4.8 (6)
H21	0.422 (5)	0.148 (4)	0.283 (6)	9.0 (10)
H22	0.519 (5)	0.174 (3)	0.497 (4)	6.5 (7)
H23	0.478 (4)	0.293 (3)	0.410 (4)	5.6 (8)

<sup>a</sup> Estimated standard deviations are in parentheses. The isotropic temperature factor is of the form  $\exp[-B(\sin^2 \theta)/\lambda^2]$ .

**Table II.** Anisotropic Thermal Parameters<sup>a</sup>

Atom	10 <sup>4</sup> β <sub>11</sub>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>
S1	143 (1)	91 (1)	150 (1)	57 (1)	19 (1)	36 (1)
B1	105 (4)	83 (3)	145 (4)	30 (3)	21 (3)	39 (3)
B2	102 (4)	64 (2)	108 (4)	23 (2)	27 (3)	17 (2)
B3	150 (4)	97 (3)	146 (4)	67 (3)	72 (4)	42 (3)
B4	105 (4)	88 (3)	183 (5)	30 (3)	28 (4)	52 (3)
B5	152 (5)	77 (3)	101 (4)	30 (3)	9 (3)	7 (2)
B6	129 (4)	73 (2)	114 (4)	44 (3)	43 (3)	12 (2)
B7	132 (4)	82 (3)	94 (3)	43 (3)	30 (3)	17 (2)
B8	131 (4)	97 (3)	148 (4)	53 (3)	58 (4)	52 (3)
B9	136 (4)	67 (2)	139 (4)	30 (3)	20 (3)	17 (2)
B10	111 (4)	77 (2)	108 (4)	41 (3)	31 (3)	24 (2)
C1	206 (5)	171 (4)	126 (4)	85 (4)	29 (4)	40 (3)
C2	171 (5)	300 (8)	232 (7)	143 (5)	65 (5)	55 (6)

<sup>a</sup> Estimated standard deviations are given in parentheses. The form of the anisotropic thermal parameter is given by  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

least-squares refinement, all nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were refined with isotropic thermal parameters. On the final cycle of refinement, no shift in any parameter was greater than 12% of the standard deviation in that parameter. This refinement lowered *R* to its final value of 0.034 and *R<sub>w</sub>* to 0.048. The error in an observation of unit weight was 1.02. Correction for extinction was not deemed necessary. A final difference Fourier electron density map exhibited no peak higher than 0.22 e Å<sup>-3</sup>.

Final atomic positional and isotropic thermal parameters are listed in Table I. Anisotropic thermal parameters are listed in Table II.

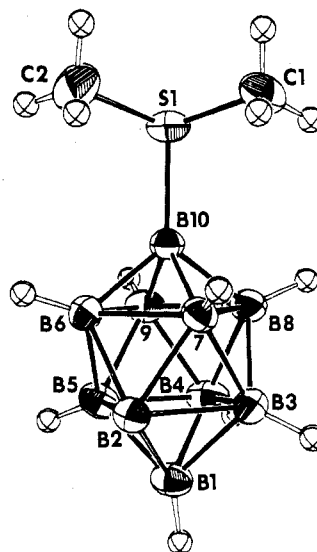
## Results and Discussion

The calculated bond lengths for 10,10'-[B<sub>10</sub>H<sub>8</sub>S(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> may be found in Table III, and calculated bond angles are given in Table IV. Standard deviations reported in these tables include contributions from the estimated errors in the unit cell parameters. Figure 1 shows the atomic numbering scheme used for nonhydrogen atoms in one of the B<sub>10</sub> halves of the dimer, while Figure 2 shows the structure of the neutral dimeric molecule. Figure 3 contains a view of the packing of the dimeric molecules within the unit cell.

**Table III.** Interatomic Distances (Å)<sup>a</sup>

(a) Involving the Intercage Linkage			
B1-B2'	1.901 (3)	B2-B2'	1.686 (4)
(b) Involving Apical Boron			
B10-B6	1.671 (3)	B1-B2	1.677 (3)
B10-B7	1.681 (3)	B1-B3	1.782 (3)
B10-B8	1.682 (4)	B1-B4	1.738 (3)
B10-B9	1.691 (2)	B1-B5	1.778 (4)
(c) Involving B-B Belt Distances			
B6-B7	1.969 (3)	B2-B3	1.873 (4)
B7-B8	1.823 (3)	B3-B4	1.813 (3)
B8-B9	1.877 (4)	B4-B5	1.813 (4)
B9-B6	1.820 (3)	B5-B2	1.876 (3)
(d) Involving B-B Interbelt Distances			
B6-B2	1.829 (4)	B8-B3	1.778 (4)
B6-B5	1.782 (3)	B8-B4	1.817 (3)
B7-B2	1.809 (3)	B9-B4	1.812 (4)
B7-B3	1.770 (4)	B9-B5	1.770 (3)
(e) Involving Sulfur			
S1-C1	1.789 (3)	S1-B10	1.861 (2)
S1-C2	1.781 (3)		
(f) Involving Hydrogen			
H1-B1	1.09 (2)	H9-B9	1.12 (2)
H3-B3	1.11 (3)	H11-C1	0.93 (4)
H4-B4	1.07 (2)	H12-C1	0.93 (4)
H5-B5	1.04 (2)	H13-C1	0.93 (3)
H6-B6	1.04 (2)	H21-C2	0.94 (5)
H7-B7	1.13 (2)	H22-C2	0.93 (3)
H8-B8	1.09 (2)	H23-C2	0.91 (3)

<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses.



**Figure 1.** View of half of the 10,10'-[B<sub>10</sub>H<sub>8</sub>(S(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>]<sub>2</sub> dimer, showing the numbering scheme employed. Hydrogen atoms (which are drawn artificially small) were numbered according to the atom to which they were attached.

The geometry of the molecule as a whole is closely related to that of the B<sub>20</sub>H<sub>18</sub><sup>2-</sup> ion,<sup>3</sup> and the general structures of the individual halves of the dimer resemble the bicapped square-antiprismatic cage structure found for the *closo*-B<sub>10</sub>H<sub>10</sub><sup>2-</sup> units in Cu<sub>2</sub>[B<sub>10</sub>H<sub>10</sub>].<sup>16</sup> Thus, the structure consists of two apically substituted (by dimethyl sulfide) fragments linked by a pair of closed, three-center B-B-B bonds involving adjacent axial and equatorial boron atoms in each B<sub>10</sub> unit.

The B2-B2' distance in the linkage between the two *closo* B<sub>10</sub> fragments is quite short at 1.686 (4) Å and may be compared with the values of 1.72 (1) and 1.65 (1) Å obtained for the corresponding distances in the disordered pair of

Table IV. Interatomic Angles (deg)<sup>a</sup>

(a) Involving the Intercege Linkage				(d) Involving Equatorial Belt Atoms Only			
B1-B2-B2'	68.9 (1)	B2'-B2-B5	106.4 (2)	B7-B6-B5	101.0 (2)	B3-B2-B7	57.4 (1)
B1-B2-B1'	124.2 (1)	B2'-B2-B7	145.5 (2)	B7-B6-B9	88.7 (1)	B3-B2-B6	103.6 (1)
B1'-B2-B3	132.4 (2)	B2'-B2-B6	147.2 (2)	B7-B6-B2	56.8 (1)	B3-B2-B5	91.2 (1)
B1'-B2-B5	134.0 (2)	B2'-B1-B3	55.8 (1)	B7-B6-B5	62.6 (1)	B7-B2-B6	65.5 (1)
B1'-B2-B7	111.6 (1)	B2'-B1-B3	100.4 (1)	B2-B6-B9	101.2 (2)	B7-B2-B5	103.7 (1)
B1'-B2-B6	112.6 (2)	B2'-B1-B4	151.5 (2)	B5-B6-B9	58.9 (1)	B6-B2-B5	57.5 (1)
B2'-B2-B1'	55.3 (1)	B2'-B1-B5	101.7 (2)	B6-B7-B8	88.4 (1)	B4-B3-B8	60.8 (1)
B2'-B2-B3	105.2 (2)			B6-B7-B3	102.0 (1)	B4-B3-B7	102.9 (2)
				B6-B7-B2	57.7 (1)	B4-B3-B2	86.8 (2)
(b) Involving Sulfur				B2-B7-B3	63.1 (1)	B8-B3-B7	61.8 (1)
C1-S1-C2	102.3 (1)	S1-B10-B7	128.2 (1)	B2-B7-B8	101.9 (1)	B8-B3-B2	101.2 (2)
C1-S1-B10	103.6 (1)	S1-B10-B8	125.4 (2)	B3-B7-B8	59.3 (1)	B7-B3-B2	59.5 (1)
C2-S1-B10	105.4 (2)	S1-B10-B9	127.8 (1)	B7-B8-B3	58.9 (1)	B5-B4-B9	58.5 (1)
S1-B10-B6	130.3 (2)			B7-B8-B4	100.6 (1)	B5-B4-B8	103.9 (2)
(c) Involving Apical Boron				B7-B8-B9	91.5 (2)	B5-B4-B3	95.3 (1)
B6-B10-B7	72.0 (1)	B2-B1-B3	65.5 (1)	B3-B8-B4	60.6 (1)	B9-B4-B8	62.3 (1)
B6-B10-B8	104.3 (2)	B3-B1-B4	62.0 (1)	B3-B8-B9	102.9 (2)	B9-B4-B3	104.1 (1)
B6-B10-B9	65.6 (1)	B4-B1-B5	62.1 (1)	B4-B8-B9	58.7 (1)	B8-B4-B3	58.6 (1)
B7-B10-B8	65.7 (1)	B5-B1-B2	101.7 (2)	B8-B9-B4	59.0 (1)	B4-B5-B9	60.7 (1)
B7-B10-B9	103.6 (2)	B2-B1-B4	95.8 (2)	B8-B9-B5	103.2 (2)	B4-B5-B6	102.8 (2)
B8-B10-B9	67.6 (1)	B3-B1-B5	97.6 (2)	B8-B9-B6	91.4 (1)	B4-B5-B2	86.7 (1)
B10-B6-B7	54.2 (1)	B1-B2-B3	59.9 (1)	B4-B9-B5	60.8 (1)	B9-B5-B6	61.6 (1)
B10-B6-B9	57.7 (1)	B1-B2-B7	114.3 (2)	B4-B9-B6	101.3 (2)	B9-B5-B2	101.3 (1)
B10-B6-B2	107.0 (2)	B1-B2-B6	114.2 (1)	B5-B9-B6	59.5 (1)	B6-B5-B2	59.9 (1)
B10-B6-B5	111.0 (2)	B1-B2-B5	59.8 (1)				
B10-B7-B6	53.8 (1)	B1-B3-B4	57.8 (1)	(e) Involving Hydrogen			
B10-B7-B8	57.2 (1)	B1-B3-B8	113.8 (2)	H1-B1-B2	152 (1)	H7-B7-B3	122 (1)
B10-B7-B2	107.5 (1)	B1-B3-B7	111.1 (2)	H1-B1-B3	130 (1)	H7-B7-B6	128 (1)
B10-B7-B3	111.1 (1)	B1-B3-B2	54.6 (1)	H1-B1-B4	112 (1)	H7-B7-B8	135 (1)
B10-B8-B7	57.1 (1)	B1-B4-B5	60.1 (1)	H1-B1-B5	124 (1)	H7-B7-B10	120 (1)
B10-B8-B3	110.6 (1)	B1-B4-B9	113.9 (2)	H1-B1-B2'	96 (1)	H8-B8-B3	118 (1)
B10-B8-B4	109.1 (2)	B1-B4-B8	114.1 (1)	H3-B3-B1	116 (1)	H8-B8-B4	120 (1)
B10-B8-B9	56.4 (1)	B1-B4-B3	60.2 (1)	H3-B3-B2	129 (1)	H8-B8-B7	132 (1)
B10-B9-B8	56.0 (1)	B1-B5-B4	57.9 (1)	H3-B3-B4	134 (1)	H8-B8-B9	131 (1)
B10-B9-B4	108.9 (2)	B1-B5-B9	114.0 (2)	H3-B3-B7	120 (1)	H8-B8-B10	122 (1)
B10-B9-B5	110.6 (1)	B1-B5-B6	111.6 (1)	H3-B3-B8	123 (1)	H9-B9-B4	122 (1)
B10-B9-B6	56.7 (1)	B1-B5-B2	54.6 (1)	H4-B4-B1	116 (1)	H9-B9-B5	121 (1)
				H4-B4-B3	129 (1)	H9-B9-B8	130 (1)
				H4-B4-B5	128 (1)	H9-B9-B6	130 (1)
				H4-B4-B8	121 (1)	H9-B9-B10	119 (1)
				H4-B4-B9	120 (1)	H11-C1-S1	108 (2)
				H5-B5-B1	119 (2)	H11-C1-H12	114 (3)
				H5-B5-B2	132 (1)	H11-C1-H13	110 (3)
				H5-B5-B4	133 (1)	H12-C1-S1	106 (2)
				H5-B5-B6	118 (1)	H12-C1-H13	108 (2)
				H5-B5-B9	120 (1)	H13-C1-S1	110 (2)
				H6-B6-B2	117 (1)	H21-C2-S1	107 (2)
				H6-B6-B5	121 (1)	H21-C2-H22	114 (4)
				H6-B6-B7	129 (1)	H21-C2-H23	112 (3)
				H6-B6-B9	136 (1)	H22-C2-S1	109 (2)
				H6-B6-B10	123 (1)	H22-C2-H23	106 (2)
				H7-B7-B2	119 (1)	H23-C2-S1	108 (2)

<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses.

$B_{20}H_{18}^{2-}$  ions in the structure of the triethylammonium salt.<sup>3</sup> This observed B2-B2' distance is quite comparable to what may be found for boron-boron two-center, two-electron bonds, as found in the structure of 2,2'-bis[1-thia-*closo*-deca-borane(8)],<sup>17</sup> where two *closo*- $B_9H_9S$  cages were linked by a direct two-center, two-electron B-B bond of length 1.678 (5) Å. The B1-B2' distance is, as expected, much longer and is found to be 1.901 (3) Å. In the disordered pair of  $B_{20}H_{18}^{2-}$  ions,<sup>3</sup> the corresponding distances were found to be 1.92 (1) and 1.86 (1) Å. Recent calculations<sup>2</sup> support the interpretation that the bonding in these linkages corresponds to a pair of closed three-center B-B-B bonds. The large H1-B1-B2 angle of 152 (1)° in the present structure (see Figure 2) suggests that the hydrogen attached to the bridging atom B1 is actually bent away from the bonding region for the cage-cage linkage, an effect that was also seen in the structure of the  $B_{20}H_{18}^{2-}$  species.<sup>3</sup>

The dimethyl sulfide group is found to be bonded to the  $B_{10}$  cages at the apical positions farthest from the intercege linkage. Although equatorially substituted isomers of this compound

are known,<sup>7</sup> substitution at the apical position of  $B_{20}H_{18}^{2-}$  not involved in bridging is predicted to be preferred for electrophilic reagents on the grounds of the calculated atomic charges within the borane anion.<sup>2</sup> The bond lengths from sulfur to boron (1.861 (2) Å) and from sulfur to carbon (average 1.785 (3) Å) are slightly shorter than normal (see below), although averaging over the thermal motion (with atoms moving independently) extends these observed values to the more normal values of 1.902 (2) Å for S1-B10 and 1.844 (3) Å for S-C(methyl). Sulfur was found to be bound to boron in an exopolyhedral position in  $B_{10}H_{12}(S(CH_3)_2)_2$ ,<sup>18</sup> where independent S-B bond lengths of 1.92 (1) and 1.93 (1) Å were observed, as well as an average S-C(methyl) bond length of 1.83 (1) Å. When the sulfur atom is present as part of the cage structure, S-B bond lengths are not found to differ greatly from those quoted above. For example, in 2,2'-bis[1-thia-*closo*-deca-borane(8)]<sup>17</sup> the average S-B distance was 1.923 (3) Å, in the metathiothiaborane  $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$  the average S-B distance was reported as 2.02 (5) Å,<sup>19</sup> and in  $B_9H_{12}S^-$  the S-B distances averaged to 1.89 (3) Å.<sup>25</sup>

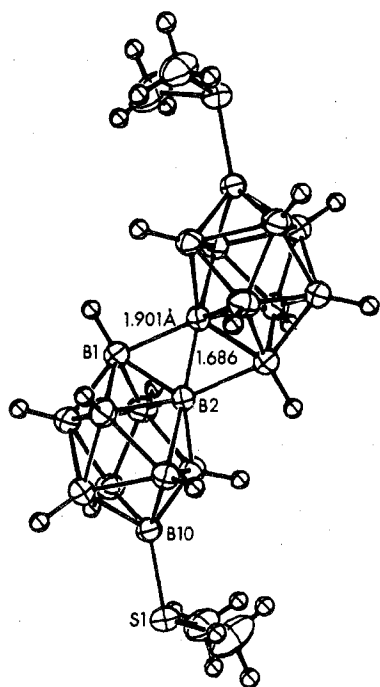


Figure 2. Overall view of the dimeric  $10,10'-[B_{10}H_8(S(CH_3)_2)_2]$  molecule, showing the nature of the intercage connection.

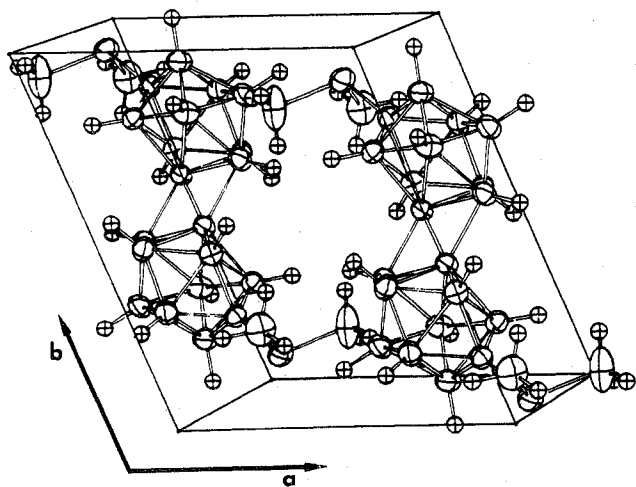


Figure 3. View of the molecular packing of  $10,10'-[B_{10}H_8(S(CH_3)_2)_2]$  within the unit cell.

The geometry of the  $B_{10}$  cage is consistent with earlier results. The four bond lengths from the apical boron atom B10 (bearing the dimethyl sulfide moiety) to the boron atoms of the "upper" equatorial belt show only slight (but possibly significant) variations about the average value of 1.681 (3) Å. These distances are, as a group, only slightly shorter than the average apex-edge B-B distances of 1.70 (9) and 1.71 (7) Å observed in  $B_{20}H_{18}^{2-}$ ,<sup>3</sup> though in this borane anion considerable variation in the individual distances was observed, presumably due to disorder. In the  $B_{10}H_{10}^{2-}$  anion,<sup>16</sup> average apex-edge B-B distances were even longer, at 1.73 (2) Å. It is possible that the slightly shortened S1-B10 bond noted above and these shortened apex-edge boron-boron distances reflect a small degree of resonance interaction between the sulfur atom and the boron cage.

Examination of other boron-boron distances within the cage reveals an interesting pattern. The distances from B1, the apical boron atom involved in the intercage linkage, to the boron atoms of the "lower" equatorial belt of the  $B_{10}$  unit, are

not all equal. The bonds to B2 and B4 are significantly different at 1.677 (3) and 1.738 (3) Å, respectively, and both are significantly shorter than the observed distances to B3 and B5 (equal within experimental error at 1.782 (3) and 1.778 (4) Å). B2, which is tightly bound to B1 and engaged in intercage linkage, then is found to form relatively weak bonds to B3 and B5 (1.873 (4) and 1.876 (3) Å), while bonds from B4 (less tightly bound to B1) to these "lower" belt atoms are significantly shorter (1.813 (3) and 1.813 (4) Å). Boron-boron bonds between the two equatorial belts occur in the range 1.770 (4)–1.829 (4) Å, with the longest bonds in this group from atoms B2 and B4 to atoms of the "upper" belt and the shortest bonds in the group connecting atoms B3 and B5 to the "upper" belt atoms. In the "upper" equatorial belt itself, the B7-B8 and B6-B9 distances are equal within experimental error at 1.823 (3) and 1.820 (3) Å, respectively, while B8-B9 at 1.877 (4) Å and B6-B7 at 1.969 (3) Å (the longest B-B distance in the cage) are significantly longer. A similar pattern of bond length variations may be discerned in the results for the  $B_{20}H_{18}^{2-}$  ion,<sup>3</sup> although strong random variations, presumably due to the disorder, appear to be superimposed on the results. In general, the B-B interatomic distances reported here compare well with results of other related studies.<sup>3,4,16,17</sup>

The variations in B-B interatomic distances reported above for the  $B_{10}$  subunit may be at least partially interpreted in terms of the localized valence structure reported recently<sup>2</sup> for the  $B_{20}H_{18}^{2-}$  ion. Thus, the B1-B2 and B1-B4 distances are expected to be short, since each of these atoms is participating in strong, three-center bonding. Boron atoms B3 and B5, however, do not participate in any three-center bonding involving B1 and B2 simultaneously and are only connected with B1 through one three-center system each. The distances from B1 to B3 and B5 would thus be expected to be longer than those to B2 and B4, in agreement with the observations. In the "lower" belt (B2-B5), B3 and B5 are linked to B4 through two three-center systems each, while simultaneously connected to B2 through only one three-center system each. Thus, distances B4-B3 and B4-B5 would be expected to be shorter than distances B2-B3 and B2-B5, again in agreement with the observations. The remainder of the localized valence scheme<sup>2</sup> is not sufficiently detailed to allow ready correlation with the pattern of interatomic distances observed in this study.

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**Supplementary Material Available:** Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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## Structures of *N*-Methylporphyrin Complexes. 3.<sup>1</sup> Chloro-*N*-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatomanganese(II)

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The crystal and molecular structure of chloro-*N*-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatomanganese(II),  $\text{Mn}(\text{N}_4\text{C}_{45}\text{H}_{31})\text{Cl}$ , has been determined from three-dimensional single-crystal x-ray diffraction data, collected by counter techniques. The dark purple crystals are triclinic, space group  $P\bar{1}$  (No. 2), with two formula units in a unit cell of dimensions  $a = 7.558$  (6) Å,  $b = 14.993$  (12) Å,  $c = 17.476$  (13) Å,  $\alpha = 103.13$  (2)°,  $\beta = 97.09$  (3)°, and  $\gamma = 94.00$  (2)°. The structure has been refined by least-squares methods to  $R = 0.072$  ( $R_w = 0.094$ ) for 3815 unique reflections with  $F^2 > 3\sigma(F^2)$ . The coordination geometry about the manganese(II) ion in the monomeric neutral complex is based on a distorted square pyramid. Three of the four basal coordination sites are occupied by normal pyrrole nitrogen atoms of the porphyrin ligand (Mn-N = 2.118 (5), 2.156 (5), and 2.155 (6) Å), while the alkylated nitrogen occupying the fourth position forms a much longer bond to manganese (Mn-N = 2.368 (5) Å). The apical position is occupied by the chloride ion (Mn-Cl = 2.295 (3) Å). The *N*-methyl group exerts a profound influence on the overall structure, causing the *N*-alkylated pyrrole ring to deviate strongly from the mean plane of the remainder of the porphyrin ligand and blocking access to the sixth coordination site on the manganese(II) ion. The manganese(II) ion is displaced far out of the mean porphyrin plane toward the apical position and is high spin in this novel coordination environment.

### Introduction

Recent definitive structural characterizations<sup>2</sup> of manganese(II)-porphyrin systems have demonstrated that the manganese(II) ions in these systems prefer to be high-spin, highly displaced out of the mean plane of the macrocycle, and five-coordinate. Interest in the study of manganese(II) porphyrins arises from the recent observation<sup>3</sup> of reversible binding of dioxygen by a synthetic manganese(II) porphyrin complex, *meso*-tetraphenylporphyrin(pyridine)manganese(II). Earlier studies on manganese(II)-porphyrin systems have included studies on incorporation of manganese porphyrins into protein systems.<sup>4,5</sup>

We have recently undertaken systematic synthetic, mechanistic, and structural studies of transition metal complexes of *N*-methylated porphyrin ligands.<sup>1,6-9</sup> In comparison with normal porphyrin systems, metal complexes of *N*-methylporphyrins show strong tendencies toward five-coordination, with large out-of-plane displacements of the metal ion, due to the strong stereochemical influence of the *N*-methyl group.<sup>1,10</sup> The geometric and electronic constraints attendant upon *N*-alkylation may allow these complexes to serve as models for the possible "sitting-atop" complexes which have been discussed as intermediates in metalation reactions of normal porphyrins.<sup>11</sup>

As one of the members of this series of complexes, the detailed structure of chloro-*N*-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatomanganese(II) has been determined by single-crystal x-ray diffraction methods. Manganese(II) in this complex is high-spin ( $\mu_{\text{eff}} = 5.9 \pm 0.1 \mu_B$  at 23 °C),<sup>9</sup> as is also the case with the manganese(II) complexes of nonmethylated *meso*-tetraphenylporphyrin.<sup>2</sup> In the complexes of the "planar"<sup>12</sup> porphyrins with manganese(II), the manganese ion is found out of the plane of the macrocycle to a large extent,<sup>2</sup> as a consequence of the high-spin electronic configuration. The degree of this out-of-plane displacement of the manganese(II) ion due to the electronic configuration about manganese will be compared in the present study with the large out-of-plane

displacement required by the steric presence of the *N*-methyl group.

### Experimental Section

The synthesis and analytical characterization of chloro-*N*-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatomanganese(II) has been previously reported.<sup>9</sup> The magnetic moment,  $\mu_{\text{eff}}$ , of the title compound was determined to be  $5.9 \pm 0.1 \mu_B$  at 23 °C (Faraday method,  $\text{Hg}[\text{Co}(\text{NCS})_4]$  calibrant, Cahn Research magnetic susceptibility system). A single crystal of the compound was characterized by x-ray fluorescence using a scanning electron microscope, and peaks characteristic of manganese and chlorine were observed.<sup>13</sup>

**Crystal Data.** For  $\text{Mn}(\text{N}_4\text{C}_{45}\text{H}_{31})\text{Cl}$  (mol wt 718.12, triclinic),  $a = 7.558$  (6) Å,  $b = 14.993$  (12) Å,  $c = 17.476$  (13) Å,  $\alpha = 103.13$  (2)°,  $\beta = 97.09$  (3)°,  $\gamma = 94.00$  (2)°,  $V = 1903.9$  Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.25$  g cm<sup>-3</sup>,  $Z = 2$ , and  $F(000) = 742$ ; space group  $P\bar{1}$ , Mo  $K\alpha$  radiation,  $\lambda_1$  0.709 30 Å,  $\lambda_2$  0.713 59 Å, and  $\mu(\text{Mo } K\alpha) = 4.72$  cm<sup>-1</sup>.

**Data Collection and Reduction.** Preliminary Weissenberg and precession photographs revealed only Laue symmetry  $\bar{1}$ , consistent with the space groups  $P1$  and  $P\bar{1}$ .<sup>14</sup> The photographs also showed that the crystal structure of the manganese(II) *N*-methyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin complex was isomorphous with that of the corresponding cobalt(II) complex (see cell parameters reported above and ref 1). Due to this strong similarity in lattice spacings and symmetry, the centric space group  $P\bar{1}$  was chosen for all further structural work with this compound.

The large, dark purple crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the  $a$  axis approximately coincident with the diffractometer  $\phi$  axis. After accurate centering, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations on the automatically determined<sup>15</sup>  $2\theta$ ,  $\chi$ , and  $\phi$  settings of 27 reflections (at ambient temperature, 20 ( $\pm$ 1) °C) with  $2\theta$  values in the range 16–25°.

The intensities of 6616 unique reflections with  $3.00^\circ < \theta < 25.00^\circ$  were measured by  $\theta$ - $2\theta$  scans, employing Zr-filtered Mo  $K\alpha$  radiation. At  $\theta$  values less than 3°, reflections were cut off on the low- $\theta$  side by the beam stop. The scan range employed was 1.2° (in  $2\theta$ ) to either side of the calculated  $K\alpha$  peak position, at a constant scan rate of 10° min<sup>-1</sup>. The number of times a given reflection was scanned varied according to the intensity, with weak reflections being scanned a