It is worth pointing out that the J values for the equilateral triangular model are slightly lower than those shown[24] by the basic iron(III) carboxylates which possess the Fe_3O triangular oxy-bridged unit.[27]

The $S = {}^5/_2$ Fisher infinite-chain model gave quite good agreement for the compound $FeOHSO_4$, which is to be expected in view of the crystal structure.[4] Mössbauer effect measurements on this compound show[30] an antiferromagnetic ordering temperature of *ca.* 80°K at which a quadrupole doublet is replaced by a six-line hyperfine spectrum. Application of the Fisher model to the amine sulfate complexes gave moderate agreement for complex B but very poor agreement for the other complexes.

The results of the magnetic studies of the iron(III)–amine–sulfate complexes therefore suggest that the basic unit of the polynuclear structure is possibly a trinuclear cluster of interacting $S = {}^5/_2$ iron(III) ions. On the basis of chemical and physical evidence given previously, together with the relationship to $FeOHSO_4$, it is suggested that the bridging is through hydroxy groups and not through oxy linkages as found with certain other basic ferric complexes.[15] Trinuclear hydroxy-bridged clusters have, in fact, been characterized in some hydrolyzed tin(II) and beryllium(II) species.[31]

In order further to test the applicability of the simple trinuclear cluster model to the present compounds, we are currently extending the susceptibility measurements down to 4°K together with field-dependent magnetization studies.

Acknowledgment.—K. I. P. is grateful to the Victorian Public Service and to the School of Physical Sciences, La Trobe University, for financial support.

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(30) B. D. Rumbold, to be submitted for publication.

(31) D. L. Kepert, *Proc. Roy. Aust. Chem. Inst.*, **37**, 135 (1970), and references therein.

CONTRIBUTION NO. 2699 FROM THE DEPARTMENT OF
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The Degradation of Biscarborane

BY M. F. HAWTHORNE,* D. A. OWEN, AND J. W. WIGGINS

Received September 1, 1970

It has been observed that 1,2-dicarba-*closo*-dodecaborane(12) and its B- and C-substituted derivatives are degraded by ethanolic potassium hydroxide to give the corresponding 7,8-dicarba-*nido*-dodecahydroundecaborate(1−) ion and its B- and C-substituted derivatives with evolution of 1 mol equiv of hydrogen[1-4]

$$1,2\text{-}B_{10}C_2H_{12} + OH^- + 3C_2H_5OH \xrightarrow[15\ \text{hr}]{80^\circ} 7,8\text{-}B_9C_2H_{12}^- + H_2O + B(OC_2H_5)_3 + H_2$$

We have found that biscarborane[5] {1-[1′-1′,2′-dicarba-*closo*-dodecaborane(12)]-1,2-dicarba-*closo*-dodecaborane(12)} is selectively degraded by ethanolic potassium hydroxide at reflux for 1.5 hr to give initially 1 mol equiv of hydrogen and 7-[1′-1′,2′-dicarba-*closo*-dodecaborano(12)]-7,8-dicarba-*nido*-dodecahydroundecaborate(1−) (I), which may be isolated or further degraded by ethanolic potassium hydroxide at reflux for 120 hr to give a second mole equivalent of hydrogen and 7-(7′-7′,8′-dicarba-*nido*-dodecahydroundecaborato)-7,8-dicarba-*nido*-dodecahydroundecaborate(2−) (II)

$$1\text{-}(1'\text{-}1',2'\text{-}B_{10}C_2H_{11})\text{-}1,2\text{-}B_{10}C_2H_{11} + OH^- + 3C_2H_5OH \xrightarrow[1.5\ \text{hr}]{80^\circ} 7\text{-}(1',1',2'\text{-}B_{10}C_2H_{11})\text{-}7,8\text{-}B_9C_2H_{11}^-\ (\text{I}) + H_2O + B(OC_2H_5)_3 + H_2$$

$$\text{I} + OH^- + 3C_2H_5OH \xrightarrow[120\ \text{hr}]{80^\circ} 7\text{-}(7'\text{-}7',8'\text{-}B_9C_2H_{11})\text{-}7,8\text{-}B_9C_2H_{11}^{2-}\ (\text{II}) + H_2O + B(OC_2H_5)_3 + H_2$$

I and II were conveniently isolated in 80% yield as their cesium or quaternary ammonium salts, which were conveniently purified by recrystallization from hot water or water–ethanol.

The 60-MHz ^{1}H nmr spectrum of the cesium salt of I in deuterioacetone consisted of two broad singlets of equal intensity at τ 8.3 and 6.1, which were assigned with confidence to the 8 and 2′ carborane protons, respectively, by comparison with the resonances observed in the spectra of biscarborane[5] and Cs-7,8-$B_9C_2H_{12}$.[3] The 80-MHz ^{11}B nmr spectrum of I in acetone is presented in Figure 1. At least ten different types of boron environments (a–j) could be distinguished. Two high-field doublets of intensity 1.0 (i, j) were very similar to features attributed to the 10 and 1 boron atoms in the spectrum of 7,8-$B_9C_2H_{12}^-$ and its C-substituted derivatives. The spectrum contained another high-field doublet of intensity 1.0 (h) and a low-field set of at least seven other doublets of total intensity 16. These ten observed unique boron environments of total intensity 19 correspond nicely to the 15 unique boron en-

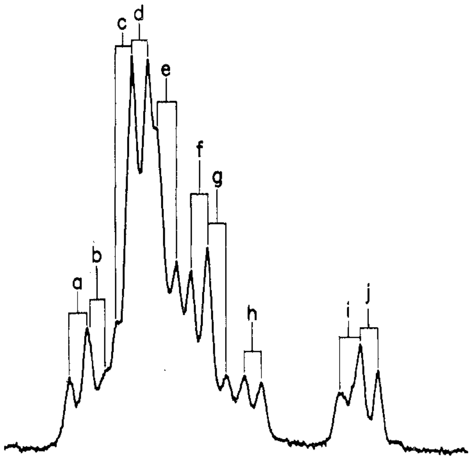

Figure 1.—An 80-MHz ^{11}B nmr spectrum of Cs-7-(1′-1′,2′-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}$ in acetone. Chemical shifts, relative to external $BF_3 \cdot O(C_2H_5)_2$ (coupling constants, Hz): (a) +5.2 (158), (b) +7.2 (136), (c) +10.0 (138), (d) +11.8 (145), (e) +14.7 (161), (f) +18.1 (152), (g) +20.0 (152), (h) +23.7 (140), (i) +34.0 (140), (j) +36.3 (158).

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(2) M. F. Hawthorne and P. A. Wegner, *ibid.*, **87**, 4392 (1965).

(3) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

(4) M. F. Hawthorne and P. A. Wegner, *ibid.*, **90**, 986 (1968).

(5) J. A. Dupont and M. F. Hawthorne, *ibid.*, **86**, 1643 (1964).

vironments of total intensity 19 expected for I. From these ^{1}H and ^{11}B nmr data, we tentatively propose the structure in Figure 2 for I, wherein the icosahedral 1′,2′-$B_{10}C_2H_{11}$ group is bound through a C(1′)–C(7) bond to the 7,8-$B_9C_2H_{11}^-$ moiety. This structure is similar to that proposed for the bipolyhedral ions containing 2′-R′-1′,2′-$B_{10}C_2H_{10}$ (R′ = H, CH_3) groups and a 7,9-$B_9C_2H_{11}^-$ moiety.[6,7]

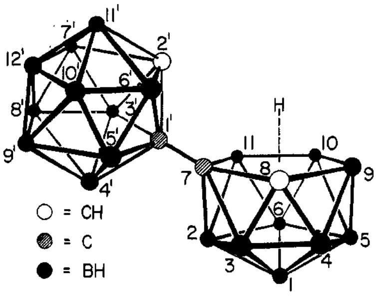

Figure 2.—The proposed structure and numbering system for the 7-(1′-1′,2′-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}^-$ ion.

Further reaction of I with ethanolic KOH at reflux for 120 hr, followed by isolation of the product as the cesium or trimethylammonium salt, afforded an 80% yield of the dicesium salt of II. The 60-MHz ^{1}H nmr spectrum in deuterioacetone of this salt consisted of a single broad singlet at τ 8.2, which was assigned to the equivalent 8 and 8′ carborane protons. The 80-MHz ^{11}B nmr spectrum of II in acetone is presented in Figure 3. It consisted of a set of at least eight different doublets (a–h) and was strikingly similar to the spectrum of asymmetrically 7-substituted 7,8-$B_9C_2H_{11}^-$ ions.[3] It contained the two familiar high-field doublets (g, h) of intensity 1 and a set of six (a–f) overlapping doublets of total intensity 7.2 at lower field. From this ^{1}H and ^{11}B nmr evidence, we tentatively propose the structure in Figure 4 for II, where the two equivalent 7,8-$B_9C_2H_{11}^-$ and 7′,8′-$B_9C_2H_{11}^-$ groups are joined by a C(7)–C(7′) bond. This would represent the first example of a bipolyhedral ion consisting of two connected negatively charged icosahedral carborane fragments. Two isomeric representations for II are possible, depending upon whether boron atom 3′ or 6′ of I (Figure 2) is removed by degradation. Removal of boron atom 3′ affords the isomer of II depicted in Figure 4, while removal of boron atom 6′ of I affords the isomeric derivative, where boron atom 11′ in Figure 4 becomes carbon 8′, etc. Due to electron–electron and carbon–carbon repulsion considerations, we tentatively propose II to be the more stable of the two isomers and the one expected to be formed.

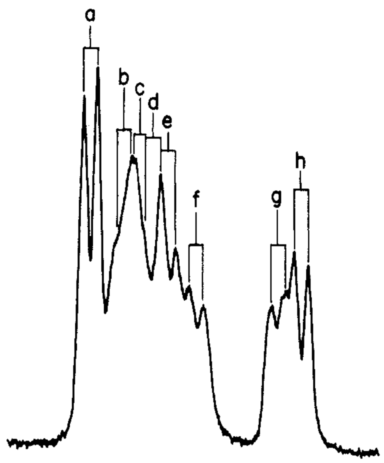

Figure 3.—An 80-MHz ^{11}B nmr spectrum of Cs_2-7-(7′-7′,8′-$B_9C_2H_{11}$)-7,8-$B_9C_2H_{11}$ in acetone. Chemical shifts, relative to external $BF_3 \cdot O(C_2H_5)_2$ (coupling constants, Hz): (a) +11.3 (150), (b) +15.4 (148), (c) +17.6 (129), (d) +18.9 (142), (e) +20.5 (137), (f) +24.0 (135), (g) +33.8 (148), (h) +36.4 (132).

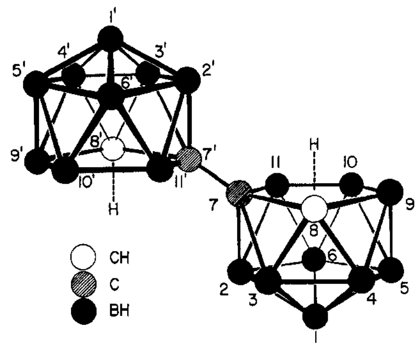

Figure 4.—The proposed structure and numbering system for the 7-(7′-7′,8′-$B_9C_2H_{11}$)-7,8-$B_9C_2H_{11}^{2-}$ ion.

Investigation of the possibility of incorporating transition metal ions into the open faces of I and II, by conversion of I and II to the corresponding 2 and 4 ions which may be prepared by treatment of I and II with sodium hydride, is under way.

Experimental Section

Methods and Materials.—Biscarborane [1-(1′-1′,2′-$B_{10}C_2H_{11}$)-1,2-$B_{10}C_2H_{11}$] was prepared by literature methods[5] and was recrystallized from hot reagent grade acetonitrile before use. All other reagents were used as supplied. All reactions involving biscarborane and its derivatives were performed under nitrogen atmospheres. Infrared spectra were obtained as Nujol mulls using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. The 60-MHz ^{1}H nmr spectra were obtained using a Varian A-60 nmr spectrometer, while 80-MHz ^{11}B nmr spectra were obtained using an experimental spectrometer designed and constructed by Professor F. A. L. Anet. Elemental analyses were made by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

7-(1′-1′,2′-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}^-$.—In a 500-ml round-bottom flask equipped with a reflux condenser topped by a nitrogen inlet, a heating mantle, and a magnetic stirring motor was placed 2.9 g (10.1 mmol) of biscarborane, 1.40 g (25 mmol) of KOH, 200 ml of absolute ethanol, and a Teflon-coated magnetic stirring bar. The reaction mixture was refluxed for 1.5 hr and was cooled, filtered, and rotary evaporated to near dryness. The oily solid so obtained was dissolved in water to give a clear solution of the potassium salt. The cesium salt was precipitated by addition of 50 ml of 50% CsCl solution to the potassium salt. Recrystallization of the white precipitate from 50 ml of hot water afforded 2.82 g (7 mmol, 69%) of white needles of Cs-7-(1′-1′,2′-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}$, mp >360°. The tetramethylammonium salt was precipitated by adding a solution of 50 ml of 50% $(CH_3)_4NCl$ in water to the aqueous solution of the potassium salt. It was recrystallized from hot ethanol–water to give 81% of white plates of $(CH_3)_4N$-7-(1′-1′,2′-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}$, mp >360°. The infrared spectrum of a Nujol mull of this salt contained absorptions at 3060 (w), 2560 (sh, s), 2500 (vs), 1472 (s), 1452 (m), 1279 (w), 1199 (m), 1140 (w), 1125 (w), 1070 (m), 1039 (sh), 1020 (m), 952 (s), 928 (w), 796 (w), 739 (sh), 728 (m), and 706 cm^{-1} (w). *Anal.* Calcd for $B_{19}C_8H_{34}N$: B, 58.72; C, 27.47; H, 9.80; N, 4.00. Found: B, 58.52; C, 27.18; H, 9.96; N, 3.71.

7-(7′-7′,8′-$B_9C_2H_{11}$)-7,8-$B_9C_2H_{11}^{2-}$.—In a 500-ml round-bottom flask equipped as before was placed 4.2 g (10 mmol) of Cs-7-(1′-1′,2′-$B_{10}C_2H_{11}$)-7,8-$B_9C_2H_{11}$, 1.40 g (25 mmol) of KOH, 200 ml of 95% ethanol, and a Teflon-coated magnetic stirring bar.

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(6) M. F. Hawthorne and D. A. Owen, *J. Amer. Chem. Soc.*, **90**, 5912 (1968).

(7) D. A. Owen and M. F. Hawthorne, *ibid.*, **91**, 6002 (1969).

This mixture was stirred and refluxed for 120 hr, during which time hydrogen was slowly liberated. The resulting tan mixture was cooled, filtered, and rotary evaporated to dryness. The solid obtained was dissolved in 50 ml of cold water and was filtered. Addition of 100 ml of 25% CsCl solution precipitated the dianion as the cesium salt. This product was recrystallized from 85 ml of hot water to afford 4.1 g (7.7 mmol, 77%) of colorless plates of Cs_2-7-(7′-7′,8′-$B_9C_2H_{11}$)-7,8-$B_9C_2H_{11}$, dec pt >260°. The infrared spectrum of a Nujol mull contained absorptions at 3030 (w), 2500 (s), 1275 (vw), 1240 (w), 1080 (m), 1059 (m), 1032 (m), 1002 (m), 951 (w), 909 (w), 882 (w), 828 (w), 781 (m), 752 (sh), 736 (m), and 706 cm^{-1} (w). The trimethylammonium salt was prepared by addition of a solution of 50% $(CH_3)_3NHCl$ to the aqueous potassium salt, and recrystallization of the white precipitate afforded an 80% yield of $[(CH_3)_3NH]_2$-7-(7′-7′,8′-$B_9C_2H_{11}$)-7,8-$B_9C_2H_{11}$, mp 282–283° dec. *Anal.* Calcd for $B_{18}C_{10}H_{42}N_2$: B, 50.53; C, 31.19; H, 10.99; N, 7.27. Found: B, 50.42; C, 30.80; H, 11.24; N, 7.40.

Acknowledgments.—The authors wish to thank Dr. R. Wiersema and Professor F. A. L. Anet for the 80-MHz ^{11}B nmr spectra and the Office of Naval Research for its generous support of this research.

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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The Blue Solutions of Sulfur in Water at Elevated Temperatures

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Received September 14, 1970

A blue coloration developing when sulfur is heated together with water and traces of some basic salt was described by Geitner[1] in 1864. These high-temperature solutions are characterized by a strong absorption at 16.8 kK which, in analogy to the blue solutions of sulfur in aprotic, polar organic solvents,[2] is attributed to the hypersulfide ion (S_2^-) formed by the homolytic dissociation of the tetrasulfide ion. Recently a blue solution obtained by electrochemical reduction of elemental sulfur[3] in dimethyl sulfoxide was ascribed to the formation of a S_8^- species. The absorption spectra of these solutions with a strong band at 16.2 kK are very similar to that of the S_2^- ion in dimethylformamide;[2] therefore, the possibility of a S_8^- ion being formed in aqueous polysulfide solutions at elevated temperatures is also considered.

Experimental Section

Materials.—Water was purified as described;[4] hydrogen sulfide and sodium sulfide solutions were prepared by bubbling H_2S from a tank into water or sufficiently concentrated sodium hydroxide solutions. Sodium tetrasulfide was prepared from sodium and sulfur in liquid ammonia. All solutions were prepared and handled under purified nitrogen, mainly by use of Schlenk-tube techniques.

Spectra.—The spectrophotometer used was the Zeiss PMQ II with the monochromator M4 Q III. High-temperature spectra were determined by use of a cell with a path length d of 0.14 cm as previously described.[5] All spectra were corrected for the expansion of the solutions with temperature and for the background absorption of the cell and of the solvent by subtracting the absorption of the cells filled with water or one of the polysulfide-free solutions at the respective temperature.

The polysulfide spectra were measured in a 0.2 or 0.02 M bisulfide–hydrogen sulfide solution which had been prepared by mixing 5 ml of a 2.0 M (or 0.2 M) sodium sulfide solution with 5 ml of a 0.025 M sodium tetrasulfide solution and varying amounts of 2.0 M (or 0.2 M) hydrochloric acid and water to give a total of 50 ml of solution. The pH of the resulting solution was checked with a glass electrode at room temperature. From these values pH′ at elevated temperatures was estimated by use of the relationship $\text{pH}' = \text{pH} + \text{p}K'_{a_1} - 7.0$ and the values for K'_{a_1} the first dissociation constant of H_2S at elevated temperatures.[4] The ionic strength of the less concentrated sulfide solutions was kept at 0.2 by the addition of NaCl. Because of the low and constant ionic strength, concentrations were substituted for activities in eq 3 and 4.

The pH of these polysulfide solutions varied from 4.7 to 10.6 at room temperature. At a pH below 7 the polysulfide solutions became unstable at room temperature and sulfur was precipitated. With increasing temperature, however, the range of stability of polysulfide solutions was found to extend further into the acidic field, and clear solutions containing all the zerovalent sulfur in the form of polysulfide or hypersulfide ions were obtained at a pH of 5.2 and a temperature of 170°. At pH >6 and temperatures above 150°, however, another reaction affected the stability of polysulfide solutions, when zerovalent sulfur, present as polysulfide or hypersulfide, reversibly disproportionated into colorless products. Preliminary investigations showed that both SO_3^{2-} and SO_4^{2-} ions are formed together with SH^-. The formation of thiosulfate could not yet be excluded. The small amount of hydrogen ions produced according to

$$n\text{S} + n\text{H}_2\text{O} \rightleftharpoons \text{SO}_n^{2-} + (n-1)\text{SH}^- + (n+1)\text{H}^+$$

is effectively buffered by the bisulfide–hydrogen sulfide mixture. Any direct influence of the disproportionation reaction on spectra and equilibria involving hypersulfide and polysulfide ions thus can be excluded. The position of the disproportionation equilibrium is strongly dependent on pH and temperature. The rate of the reaction is very slow at temperatures below 150°, whereas at 220° equilibrium is reached within 5 min.

The reversible changes in the concentration of zerovalent sulfur occurring at a conveniently slow rate between 160 and 180° and caused by the second reaction were used to determine $\bar{n}$, the average number of zerovalent sulfur atoms per polysulfide ion as outlined below. It was assumed that the amount of S_2^- ions formed at a given temperature depends only on the total concentration of zerovalent sulfur S(0) present in the form of polysulfide and hypersulfide ions. By keeping the temperature at 160–180° zerovalent sulfur is used up by the disproportionation reaction until a state of equilibrium which depends on the pH of the solution is reached. By lowering the temperature most of S(0) can be regenerated, thus allowing the concentration of S(0) in the solution to be varied at will.

The concentration of S_2^- ions was determined by use of a molar absorptivity of 2400 as determined for the strong band at 16.2 kK in organic solution[2] at room temperature. The slight shift in $\nu_{\max}$ from 16.2 kK in dimethylformamide to 16.8 kK in water is assumed to be due to the difference in polarity of the two solvents.

If the oscillator strength of this band is presumed to remain constant with temperature and changing solvent, a lower value for the molar absorptivity should have been used as the width of the band in water at 160° was found to be 3.4 kK as compared to 2.8 kK in DMF at 20°. In the calculation of $\text{p}K'_\text{d}$ only the ratio $\epsilon_{\text{S}_3\text{S}^{2-}}/\epsilon_{\text{S}_2^{-2}}$ is of significance; thus changes in $\epsilon_{\text{S}_2^-}$ were assumed to be partly compensated for by a corresponding change in $\epsilon_{\text{S}_3\text{S}^{2-}}$. Neither the nature nor the molar absorptivities of the polysulfide ions present in aqueous solution at elevated temperatures are known. From the data given by Teder[6] for 25 and 80°, however, it was concluded that in solutions of low pH and a low ratio of S(0) to sulfide sulfur (0.04–0.4 in the present study) the molar absorptivities for these polysulfide ions can be approximated by the relationship $\epsilon_{\text{S}_{\bar{n}}\text{S}^{2-}} = \epsilon_{\text{S(0)}}\bar{n}$. With a value of 350 for $\epsilon_{\text{S(0)}}$, the molar absorptivity at 25.0 kK per atom of zerovalent sulfur, the average concentration of a mixture of polysulfides thus becomes

$$c_{\text{S}_{\bar{n}}\text{S}^{2-}} = A_{25}/350\bar{n}d \qquad (1)$$

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