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Crystal Structure and Molecular Geometry of [Me₄N⁺][Me₂B₁₀C₂H₁₁⁻], Including the Refinement of Positional and Anisotropic Thermal Parameters for All Hydrogen Atoms

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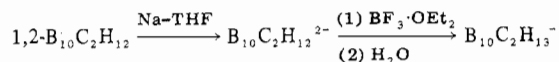*Received June 15, 1973*

The species tetramethylammonium C,C'-dimethylundecahydrodicarba-*nido*-dodecaborate, [Me₄N⁺][Me₂B₁₀C₂H₁₁⁻], crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with $a = 12.5820$ (12), $b = 12.2241$ (13), $c = 11.0005$ (10) Å, $\beta = 90.81$ (1)°, and $Z = 4$. All atoms, including hydrogens, have been accurately located from an X-ray diffraction study based on counter data collected with a Picker FACS-1 diffractometer. Following completion of the refinement of positional and anisotropic thermal parameters for all atoms (including hydrogens), the discrepancy indices are $R_F = 6.22\%$ and $R_{wF} = 3.63\%$ for 2981 symmetry-independent reflections representing data complete to $2\theta = 50°$ (Mo Kα radiation). The Me₂B₁₀C₂H₁₁⁻ anion has (noncrystallographic) C_s symmetry, with ten borons and one carbon defining an icosahedral fragment with an open B₄C face. The second carbon atom of the dicarba-*nido*-dodecaborate framework bridges two boron atoms in the open B₄C face and is bound to an exo methyl group and to an endo hydrogen. Bond distances in the Me₂B₁₀C₂H₁₁⁻ anion (in Å) are B-B = 1.726 (2)-1.867 (2), B-C = 1.624 (2)-1.672 (2), C-Me = 1.518 (2)-1.520 (2), B-H = 1.087 (10)-1.145 (10), C(cage)-H = 0.957 (9), and C(methyl)-H = 0.930 (14)-0.995 (11); within the Me₄N⁺ cation, distances are N-Me = 1.476 (2)-1.489 (2) and C-H = 0.922 (13)-1.038 (12).

Introduction

We have recently reported[1] the crystal structure of (π-C₅H₅)Co(π-7,9-B₁₀C₂H₁₂) in which the B₁₀C₂Co framework defines a 13-vertex (1, 5, 6, 1) docosahedron [=22-sided figure], the cobalt atom being linked to a cyclic belt of six atoms (four borons and two carbons). We suggest that the corresponding free B₁₀C₂H₁₂²⁻ ion will have a "nido" structure with an open B₄C₂ face. The B₁₀C₂H₁₂²⁻ ion and its monoprotonated derivative, B₁₀C₂H₁₃⁻, may be prepared as shown in Scheme I.[2] We have recently become interested in deter-

Scheme I

$$1,2\text{-}B_{10}C_2H_{12} \xrightarrow{\text{Na-THF}} B_{10}C_2H_{12}{}^{2-} \xrightarrow[\text{(2) H}_2\text{O}]{\text{(1) BF}_3\cdot\text{OEt}_2} B_{10}C_2H_{13}{}^{-}$$

mining the molecular geometry of the B₁₀C₂H₁₃⁻ ion or of one of its C,C'-disubstituted derivatives, R₂B₁₀C₂H₁₁⁻, in order to determine the structural relationship of these species to the B₁₀C₂H₁₂²⁻ ion.

An initial attempt to determine the crystal structure of [Ph₄As⁺][B₁₀C₂H₁₃⁻] was discontinued as soon as the unit cell constants and space group[3] were determined, since they require the carborane anion to lie in a crystallographic 4 or $\bar{4}$ (C_4 or S_4) axis, thereby indicating a severe disorder problem.

Subsequent efforts were directed toward an X-ray structural analysis of a salt of the C,C'-dimethyl anion, *i.e.*, [Me₄N⁺]·[Me₂B₁₀C₂H₁₁⁻].[2] Prior to the completion of our analysis we learned of a diffraction study of the related species [Me₄N⁺][Ph₂B₁₀C₂H₁₁⁻], by Tolpin and Lipscomb.[4]

We have now completed our structural study of [Me₄N⁺]·[Me₂B₁₀C₂H₁₁⁻] and our results are reported below. We may note that estimated standard deviations on bond lengths are extremely small with values of ~0.002 Å for B-B, B-C,

and C-N distances, 0.009-0.011 Å for B-H distances, and 0.009-0.016 Å for C-H distances.

Collection and Treatment of the X-Ray Diffraction Data

Colorless crystals of [Me₄N⁺][Me₂B₁₀C₂H₁₁⁻] were kindly provided by Professor M. F. Hawthorne of the University of California at Los Angeles. The crystal selected for the diffraction study was glued to the tip of a Pyrex glass fiber which was fixed into a brass pin on a eucentric goniometer. The crystal was a hexagonal plate between {100} faces, 0.260 mm apart, bounded by {010}, 0.348 mm apart, and {011} at distances of 0.216 mm (011), 0.183 mm (01$\bar{1}$), 0.208 mm (0$\bar{1}$1), and 0.232 mm (0$\bar{1}\bar{1}$) from an origin centered with respect to the previous two sets; the maximum dimension was 0.544 mm, parallel to c^*.

Preliminary precession and cone-axis photographs gave approximate cell dimensions, indicated C_{2h} (2/m) Laue symmetry, and exhibited the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14).[5]

The crystal was transferred to Picker FACS-1 computer-controlled diffractometer, was accurately centered, and was orientated so as to place c^* precisely coincident with the instrumental ϕ axis. The apparatus and experimental technique have been described previously.[6] Details specific to the present analysis are as follows.

Employing "high-resolution" conditions,[6] the 2θ, ω, and χ settings of the resolved Mo Kα_1 peaks of twelve high-angle ($2\theta = 34-47°$) reflections which were well dispersed in reciprocal space were determined automatically.[7] These values were used in a least-squares refinement of cell parameters and orientation parameters, using λ(Mo Kα_1) 0.70926 Å ; maximum and root-mean-square angular disagreements were 0.019 and 0.009°, respectively. The resulting unit cell parameters (at 21.5 ± 0.5°) and estimated standard deviations are $a = 12.5820$ (12) Å, $b = 12.2241$ (13) Å, $c = 11.0005$ (10) Å, and $\cos \beta = -0.01407$ (15), which corresponds to $\beta = 90.81$ (1)°. The unit cell volume is $V = 1691.75$ (34) Å³. The observed density ($\rho_{obsd} = 0.970$ (5) g cm⁻³, by neutral buoyancy in C₆H₆–CCl₄) is in agreement with that calculated for mol wt 247.44 and $Z = 4$ ($\rho_{calcd} = 0.971$ g cm⁻³). No *crystallographic* symmetry is imposed upon either the Me₂B₁₀C₂H₁₁⁻ anion or the Me₄N⁺ cation.

Employing a 3.5° takeoff angle to the X-ray tube anode and a niobium β filter (~47% transmission of Mo Kα radiation) at the de-

(1) M. R. Churchill and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 1326 (1972).

(2) G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 899 (1972); *J. Amer. Chem. Soc.*, **95**, 3174 (1973).

(3) Crystallographic parameters for [Ph₄As⁺][B₁₀C₂H₁₃⁻] are as follows: tetragonal, space group $P4/n$ [No. 85], $a = 13.68$ (2) Å, $c = 7.44$ (1) Å, $V = 1393$ (5) Å³, $\rho_{obsd} = 1.257$ (5) g cm⁻³, $\rho_{calcd} = 1.241$ g cm⁻³ for $Z = 2$.

(4) E. I. Tolpin and W. N. Lipscomb, *J. Chem. Soc., Chem. Commun.*, 257 (1973).

(5) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965, p 99.

(6) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).

(7) Diffractometer routines such as crystal orientation, centering of reflections, least-squares refinement of cell dimensions, and θ–2θ scan routines were performed by programs described by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967), and adapted by Picker Corp. to the PDP-8/I which forms an integral part of the FACS-1 system.

tector aperture (6 mm × 6 mm, 330 mm from the crystal), intensity data were collected by executing a coupled θ(crystal)-2θ(counter) scan from 0.4° in 2θ below the Mo Kα_1 peak to 0.4° in 2θ above the Mo Kα_2 peak, the scan rate being 1.0°/min.[8] Stationary-background counts, each of 20-sec duration, were recorded at the two extremes of the scan.

Before collecting the data set, the strong 002 reflection was measured (by a θ-2θ scan) at χ = 90° and at 10° intervals of ϕ from ϕ = 0° to ϕ = 350°. The intensity varied approximately as a constant + |sin ϕ| with a variation in intensity [(maximum − minimum)/average] of 22%. However, this effect cannot be due to absorption (μ(Mo Kα) = 0.496 cm^{-1}) and is attributed to secondary extinction. Confirmation of this assignment comes from the absence of any detectable ϕ dependence for the weaker 008 reflection. In addition, when the 002 "ϕ scan" was repeated 2 weeks later (following the completion of data collection), the same sinusoidal ϕ variation with reduced amplitude (now only 7.7%) was observed and greater intensity was found at all ϕ values; *i.e.*, the crystal mosaicity had increased (*vide infra*).

Data for the crystal structure analysis were collected in three batches, as follows.

(1) All reflections with 2θ < 10° were measured (full sphere; four equivalent forms) at reduced (2 mA) tube current. The tube current was returned to its usual 16 mA and all reflections whose peak counting rates did not exceed ~10,000 counts/sec at the higher current setting were remeasured (including systematic absences). Comparison of the 10 strongest equivalent sets that were measured at both current settings provided an accurate scaling factor and verified counter linearity up to ~10,000 counts/sec.

(2) All reflections of the type hkl and $\bar{h}kl$ in the range 10° < 2θ < 50° were measured (at 16-mA current). All were within the linear range of the counter. Three "standard reflections," in approximately orthogonal directions in reciprocal space (50$\bar{2}$, 051, 104) were measured after each batch of 48 reflections in order to monitor the stability of the crystal and counter. One reflection remained essentially constant while the other two *increased* in intensity (by 1.0 and 2.2%), the larger increase being associated with the strongest of the three reflections ($\bar{1}$04). [This provides further evidence that secondary extinction decreases as the crystal suffers slight radiation damage or aging.]

(3) Finally, the seven strongest reflections (2θ < 10°) were measured and were found to have increased in intensity by factors roughly proportional to their intensities. (The two largest increases in intensity were 29% for 200 and 18% for 10$\bar{2}$.) These data were not used in the subsequent analysis but provide final confirmation of substantial secondary extinction in the primary data set.

The intensity data were reduced[9] to observed structure factors, F_o, exactly as described previously,[6] except that the scaling factor, q, was held constant at 1.000 for the 16-mA data and 9.421 for the 2-mA (2θ < 10°) data. The "ignorance factor" (p) was set equal to 0.025. Any data with a net negative intensity were assigned an intensity of zero.

All 190 measurements corresponding to systematic absences were found to confirm the rules for $P2_1/c$ and were then discarded; the three "standard reflections" exhibited root-mean-square fluctuations about their average values of 0.8, 0.7, and 1.6%. [The true stability is better than this, since, *vide supra*, two reflections were *systematically* increasing in intensity.]

Estimated standard deviations, σ(F), were derived as indicated previously.[6] The "expected" values of R_F and R_{wF}, obtained by substituting σ(F_o) for ||F_o| − |F_c|| in their definitions,[10] were 6.55 and 2.72%, respectively. Approximately 16% of the data had |F_o| < 1σ and an additional 9% were less than 3σ. Nevertheless, *no reflections* were rejected on the grounds of being "unobserved." The philosophy and advantages of this approach have been discussed previously.[6,11,12]

Equivalent sets of reflections and a few duplicated measurements were replaced by their σ^{-2} weighted averages and assigned appropriately reduced standard deviations, subject to the condition that σ($F_o{}^2$) > 0.01$F_o{}^2$. [In 21 of the 27 cases in which all four equivalent data forms had been collected, the indicated precision of the mean was better than 1%.]

Finally, secondary extinction coefficients, β (defined below),[13] were calculated[14] for the 180 reflections whose scaled net intensity was greater than 8 × 10^4 counts (0.7% of the strongest reflection, 200). Transmission factors, T, ranged from 0.985 to 0.988 (total range 0.3%) but were not applied to the data.

$$\beta = \frac{1 + \cos^4 2\theta}{\sin 2\theta (1 + \cos^2 2\theta)} \left(\frac{-dT^{-1}}{d\mu} \right)$$

The final data set consisted of 2989 symmetry-independent |F_o| values, representing data complete to 2θ = 50°.

Solution and Refinement of the Structure

Programs used in determining the structure include FAME and MAGIC (generation of |E| values and symbolic addition, respectively, by R. B. K. Dewar and A. L. Stone), FORDAP (Fourier Synthesis, by A. Zalkin), SFIX (a much modified version of SFLS5, by C. T. Prewitt, for full-matrix least-squares), LSHF (a further modification of SFIX, by B. G. DeBoer), STAN1 (distances and angles, with estimated standard deviations, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral nitrogen, carbon, and boron were taken from the compilation of Cromer and Waber.[15] Both the real and imaginary components of anomalous dispersion were included in the structure factor calculations, using the values of Cromer and Liberman.[16] For hydrogen, the scattering factors of Mason and Robertson[17] were used initially; later in the analysis, the values of Stewart, Davidson, and Simpson[18] were found to be more appropriate (*vide infra*). The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$.

Normalized structure factor amplitudes[19] ("|E| values") were calculated and tested for large Σ_2 interactions[19] by FAME. The statistical distribution of |E| values was virtually identical with that expected theoretically for a centrosymmetric crystal. Seven reflections having large |E| values, six different parities (of h, k, l), and many Σ_2 interactions were selected for use as a starting set of reflections. Application of the symbolic addition procedure[19] by MAGIC assigned symbolic signs (in terms of those of the initial seven reflections) to 399 of the 402 reflections with |E| > 1.5, with no sign indication of less than 95% probability being accepted. One assignment of real (*i.e.*, + or −) signs to symbols had a much greater internal consistency than any other. The 399 signed |E| values resulting from this process were used as coefficients in a Fourier synthesis. The 19 largest peaks in this "E map" defined reasonable Me$_4$N$^+$ and Me$_2$B$_{10}$C$_2$H$_{11}$$^-$ skeletons and were assumed to be nitrogen, carbon, and boron atoms; the two cage carbons were presumed to be those atoms bearing methyl substituents. [This assignment is confirmed by the similar magnitude of the thermal parameters for boron and carbon atoms of the carborane anion at the termination of refinement.]

Three cycles of least-squares refinement of a scale factor and positional and isotropic thermal parameters for all nonhydrogen atoms led to R_F = 19.3% and R_{wF} = 21.1%. Two more cycles of refinement, which included a secondary extinction parameter, c, in the form shown below[13] (later changed, *vide infra*) and anisotropic tem-

$$F_{c,\text{cor}} = F_{c,\text{uncor}}(1 + c\beta F_o{}^2)^{-1}$$

perature factors for all nonhydrogen atoms, gave R_F = 15.6% and

(8) The detector aperture was certainly larger than necessary. The small scan range (~0.8° in 2θ) was selected following the study of peak profiles of several reflections well dispersed in reciprocal space and was shown to be appropriate by observing the peak profiles of reflections on a chart recorder. The mosaicity of the crystal, at the beginning of the study, is indicated by widths at half peak height of 0.24° in 2θ or 0.12° in ω for the reflection 008 (using a 1.5° takeoff angle).

(9) All data reduction and analysis was performed using the Fortran IV program REDUCE, by B. G. DeBoer.

(10) $R_F = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where the weight $w = \sigma^{-2}(F_o)$.

(11) J. A. McGinnerty, *J. Amer. Chem. Soc.*, **94**, 8406 (1972); see particularly "Refinement of the Structure" on p 8407.

(12) M. R. Churchill and K.-K. G. Lin, *Inorg. Chem.*, **12**, 2274 (1973).

(13) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); **23**, 558 (1967).

(14) Secondary-extinction coefficients and transmission factors were calculated using DRAB, a Fortran IV program, by B. G. DeBoer.

(15) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(16) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(17) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, **2**, 57 (1966).

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). The "best floated spherical H atom" values of Table II, p 3178, were used.

(19) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

Table I. Highest 22 Peaks on the Final Difference-Fourier Synthesis

No.	Approximate coords x, y, z	ρ, e Å^{-3}	Comments
1	0.265, 0.490, 0.090	0.19	B(3)–B(7)–B(8) triangle
2	0.375, 0.445, 0.135	0.18	B(4)–B(8)–C(9) triangle
3	0.225, 0.360, 0.250	0.17	B(6)–B(10)–B(11) triangle
4	0.410, 0.345, 0.140	0.16	On C(9)–Me(14) vector
5	0.360, 0.370, 0.230	0.15	B(5)–C(9)–B(10) triangle
6	0.320, 0.385, 0.315	0.15	B(5)–B(6)–B(10) triangle
7	0.400, 0.430, 0.225	0.15	B(4)–B(5)–C(9) triangle
8	0.350, 0.510, 0.120	0.15	B(3)–B(4)–B(8) triangle
9	0.330, 0.410, 0.115	0.15	Midpoint of B(8)–C(9)
10	0.265, 0.550, 0.205	0.15	B(1)–B(2)–B(3) triangle
11	0.155, 0.405, 0.145	0.15	Near B(7)–B(11) midpoint, displaced toward C(12)
12	0.375, 0.510, 0.270	0.14	B(1)–B(4)–B(5) triangle
13	0.185, 0.435, 0.270	0.14	B(2)–B(6)–B(11) triangle
14	0.235, 0.495, 0.305	0.14	B(1)–B(2)–B(6) triangle
15	0.325, 0.455, 0.325	0.14	B(1)–B(5)–B(6) triangle
16	0.120, 0.370, 0.240	0.14	Midpoint of B(11)–H(11)
17	0.165, 0.450, 0.195	0.14	B(2)–B(7)–B(11) triangle
18	0.205, 0.525, 0.145	0.13	B(2)–B(3)–B(7) triangle
19	0.465, 0.315, 0.000	0.13	Near H(14A) and H(14B)
20	0.090, 0.230, –0.015	0.13	Near H(13B) and H(13C)
21	0.245, 0.425, 0.360	0.13	On B(6)–H(6) vector
22	0.800, 0.395, 0.250	0.12	Midpoint of N–Me(2)

$R_{wF} = 17.0\%$. A difference-Fourier synthesis now revealed the positions of all 29 hydrogen atoms. Peaks corresponding to cage hydrogens ranged from 0.51 to 0.73 e Å^{-3}, while the smallest methyl hydrogen had a peak height of 0.29 e Å^{-3}. Only six peaks in the range 0.28–0.73 e Å^{-3} were not assignable to hydrogen atoms. Refinement cycles,[20] now including the variation of positional and isotropic thermal parameters for all hydrogen atoms, led to convergence at $R_F = 7.41\%$ and $R_{wF} = 5.54\%$.

Substitution of the Stewart[18] hydrogen atom scattering factors for those of Mason[17] produced improvement ($R_F = 7.13\%$ and $R_{wF} = 5.25\%$) even before refinement; the Stewart[18] scattering factors were therefore used in all subsequent processes.

Confidence in the quality of our data led us next to allow the refinement of *anisotropic* thermal parameters for all hydrogen atoms [Note that the ratio of hydrogen scattering to that of boron is 1:5 at $(\sin \theta)/\lambda = 0.0$ and 1:23.9 at $(\sin \theta)/\lambda = 0.6$ (the limit of our data). While the anisotropic thermal parameters of the hydrogen atoms may well contain a component due to aspherical electron density distribution as well as genuine thermal motion, the resultant ellipsoids and their orientations (see the figures) are quite sensible.] Two "refinement cycles"[20] led to convergence at $R_F = 6.36\%$ and $R_{wF} = 4.64\%$. The form of the secondary extinction correction was now changed to the form[13,21]

$$F_{c,\text{cor}} = F_{c,\text{uncor}}(1 + c\beta F_{c,\text{uncor}}^2)^{-1/4}$$

The changed form, with a hand-fitted value for c and no refinement gave $R_F = 6.31\%$ and $R_{wF} = 4.57\%$. The reduction in R_{wF} for the "one-dimensional hypothesis" that the new form for the extinction parameter is preferred is significant at a level of confidence far better than 99.5%, as judged by Hamilton's R-factor ratio test.[22]

Two further "refinement cycles"[20] followed by two cycles in which all positional parameters were refined while all temperature factors were held constant converged to $R_F = 6.29\%$ and $R_{wF} = 4.58\%$. [The corresponding discrepancy indices, omitting from the summations those eight reflections for which $|\Delta F|/\sigma(F) > 10$ (and which were given zero weight in the least-squares minimization process), were $R_F = 6.22\%$ and $R_{wF} = 3.63\%$.]

The standard deviation in an observation of unit weight, $[\Sigma w \cdot (|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 1.52, where the number of data (m) is 2981 and the number of parameters refined (n) is 434 $(m/n = 6.87)$. This function showed no significant dependence on either $\sin \theta$ or $|F_o|$, indicating a valid weighting scheme.

(20) Because the number of variables exceeded our program's capacity, one "refinement cycle" consisted of two steps. First, the positional and thermal parameters of the nitrogen and six methyl groups were refined; second, the positional and thermal parameters for atoms in the $B_{10}C_2H_{11}$ portion of the carborane anion were refined. Each step also included the refinement of the scale factor and the secondary extinction parameter.

(21) A. C. Larson in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 291 ff.

(22) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

Table II. Final Positional and "Equivalent Isotropic Thermal Parameters"[a] for $[Me_4N^+][Me_2B_{10}C_2H_{11}^-]$ with Estimated Standard Deviations[b]

Atom	x	y	z	B, Å^2
(A) Atoms in $Me_2B_{10}C_2H_{11}^-$ Anion				
B(1)	0.30973 (12)	0.54295 (12)	0.29738 (13)	3.69
B(2)	0.17947 (11)	0.52037 (12)	0.24343 (13)	3.64
B(3)	0.28003 (11)	0.56397 (12)	0.13936 (13)	3.62
B(4)	0.40253 (11)	0.50523 (12)	0.18451 (13)	3.74
B(5)	0.37993 (12)	0.41738 (12)	0.30628 (14)	3.95
B(6)	0.24302 (11)	0.41986 (12)	0.33836 (13)	3.76
B(7)	0.17813 (10)	0.47065 (12)	0.08945 (13)	3.32
B(8)	0.32280 (10)	0.44878 (12)	0.06270 (13)	3.55
C(9)	0.38213 (9)	0.37164 (10)	0.16307 (11)	3.74
B(10)	0.28947 (11)	0.31752 (12)	0.24494 (13)	3.77
B(11)	0.15492 (11)	0.37734 (12)	0.21794 (12)	3.44
C(12)	0.17285 (9)	0.33684 (10)	0.07748 (11)	3.47
Me(13)	0.07278 (11)	0.29512 (13)	0.01419 (14)	4.52
Me(14)	0.47198 (11)	0.29869 (13)	0.12031 (17)	5.77
H(1)	0.3261 (9)	0.6114 (10)	0.3641 (13)	5.5
H(2)	0.1137 (9)	0.5772 (8)	0.2768 (10)	4.4
H(3)	0.2761 (8)	0.6484 (9)	0.0971 (10)	4.7
H(4)	0.4805 (8)	0.5402 (9)	0.1686 (11)	4.7
H(5)	0.4423 (9)	0.3976 (9)	0.3757 (11)	5.0
H(6)	0.2108 (9)	0.4053 (9)	0.4323 (10)	4.6
H(7)	0.1188 (8)	0.5112 (9)	0.0304 (10)	3.6
H(8)	0.3480 (8)	0.4447 (9)	–0.0326 (10)	4.1
H(10)	0.2948 (8)	0.2293 (9)	0.2665 (10)	4.2
H(11)	0.0772 (8)	0.3479 (8)	0.2515 (9)	3.5
H(12)	0.2332 (7)	0.2947 (8)	0.0539 (9)	3.1
H(13A)	0.0122 (9)	0.3419 (10)	0.0289 (12)	5.4
H(13B)	0.0831 (9)	0.2896 (11)	–0.0751 (11)	5.8
H(13C)	0.0525 (10)	0.2235 (13)	0.0432 (13)	7.7
H(14A)	0.5282 (12)	0.3401 (13)	0.0796 (17)	9.8
H(14B)	0.4497 (10)	0.2440 (13)	0.0669 (15)	8.3
H(14C)	0.5013 (11)	0.2610 (13)	0.1861 (14)	8.0
(B) Atoms in Me_4N^+ Cation				
N	0.79549 (7)	0.42323 (8)	0.30506 (8)	3.72
Me(1)	0.85572 (13)	0.37687 (15)	0.41004 (14)	5.34
Me(2)	0.79587 (14)	0.34422 (13)	0.20206 (14)	5.43
Me(3)	0.84683 (14)	0.52677 (13)	0.26576 (17)	5.68
Me(4)	0.68488 (12)	0.44512 (17)	0.34078 (17)	6.85
H(1A)	0.8538 (12)	0.4324 (11)	0.4746 (13)	7.2
H(1B)	0.9237 (11)	0.3618 (12)	0.3845 (11)	7.1
H(1C)	0.8180 (12)	0.3082 (14)	0.4357 (13)	8.9
H(2A)	0.7535 (12)	0.3783 (10)	0.1298 (11)	7.1
H(2B)	0.8671 (12)	0.3359 (12)	0.1812 (13)	7.8
H(2C)	0.7583 (13)	0.2788 (10)	0.2280 (12)	8.2
H(3A)	0.8047 (12)	0.5577 (10)	0.1986 (15)	8.1
H(3B)	0.8403 (11)	0.5745 (10)	0.3373 (12)	7.3
H(3C)	0.9167 (12)	0.5040 (12)	0.2446 (15)	8.2
H(4A)	0.6488 (9)	0.4725 (13)	0.2700 (14)	7.3
H(4B)	0.6865 (11)	0.4953 (14)	0.4051 (14)	8.4
H(4C)	0.6508 (11)	0.3761 (14)	0.3634 (15)	8.5

[a] "Equivalent isotropic thermal parameters" correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid. [b] Estimated standard deviations, shown in parentheses, are right adjusted to the last digit of the preceding number and are derived from the inverse of the final least-squares matrix.

Final shifts of parameters were as follows: $\Delta/\sigma < 0.06$ for all positional parameters of nonhydrogen atoms, $\Delta/\sigma < 0.14$ for all positional parameters of hydrogen atoms, $\Delta/\sigma < 0.85$ for all nonhydrogen atom thermal parameters, $\Delta/\sigma < 1.28$ for all hydrogen atom thermal parameters.

The final value for the secondary extinction parameter, c, was $0.345 (11) \times 10^{-4}$ mm^{-1} e^{-2}. The maximum amounts by which F_c^2 values were reduced were (in order) 39% for the reflection 200, 31% for 021, 30% for $\overline{1}02$, 27% for 002, 22% for 020, and 14% for 220.

A final difference-Fourier synthesis, based on all 2989 data, was found to have no feature greater than 0.19 e Å^{-3} present. Nevertheless, many of the highest peaks on this map are centered on, and just exterior to, the triangular faces of the icosahedral cage. (See Table I.) Possible explanations for this observation include the following: (1) these peaks truly represent residual electron density and provide direct evidence for the distribution of bonding electrons or (2) these

Table III. Anisotropic Thermal Parameters^a with Esd's ^{b} for [Me$_4$N$^+$][Me$_2$B$_{10}$C$_2$H$_{11}$$^-$]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^c$
			(A) Atoms in Me$_2$B$_{10}$C$_2$H$_{11}$$^-$ Anion				
B(1)	4.44 (7)	3.44 (7)	3.18 (7)	−0.85 (6)	0.18 (6)	−0.21 (6)	0.192, 0.202, 0.250
B(2)	3.82 (7)	3.66 (7)	3.47 (6)	0.05 (6)	0.62 (6)	−0.49 (6)	0.189, 0.219, 0.235
B(3)	4.24 (7)	3.20 (7)	3.41 (7)	−0.15 (6)	0.23 (5)	0.30 (6)	0.193, 0.214, 0.233
B(4)	3.56 (7)	3.98 (7)	3.69 (7)	−0.67 (6)	0.12 (6)	0.17 (6)	0.196, 0.217, 0.238
B(5)	3.86 (7)	4.19 (8)	3.78 (7)	−0.67 (6)	−0.76 (6)	0.48 (6)	0.195, 0.213, 0.258
B(6)	4.20 (7)	4.09 (7)	2.98 (6)	−1.13 (6)	−0.04 (6)	0.31 (6)	0.189, 0.200, 0.259
B(7)	3.18 (6)	3.62 (7)	3.15 (6)	0.42 (5)	−0.04 (5)	0.09 (6)	0.191, 0.201, 0.222
B(8)	3.32 (6)	4.17 (7)	3.18 (6)	−0.12 (5)	0.49 (5)	−0.05 (6)	0.188, 0.215, 0.231
C(9)	3.07 (5)	3.75 (6)	4.38 (6)	0.21 (4)	−0.20 (5)	−0.21 (5)	0.194, 0.217, 0.239
B(10)	4.07 (7)	3.09 (7)	4.12 (7)	−0.22 (6)	−0.83 (6)	0.48 (6)	0.191, 0.205, 0.255
B(11)	3.09 (6)	3.88 (7)	3.35 (7)	−0.48 (5)	0.14 (5)	0.09 (6)	0.189, 0.207, 0.228
C(12)	3.10 (6)	3.57 (6)	3.73 (6)	0.24 (5)	−0.11 (5)	−0.30 (5)	0.195, 0.207, 0.226
Me(13)	3.76 (7)	4.94 (9)	4.83 (9)	0.03 (7)	−0.78 (7)	−0.98 (8)	0.200, 0.235, 0.277
Me(14)	3.93 (9)	5.80 (12)	7.57 (14)	1.29 (8)	−0.49 (9)	−1.27 (10)	0.203, 0.264, 0.329
H(1)	6.4 (7)	4.8 (7)	5.2 (8)	−2.0 (6)	0.8 (6)	−1.6 (7)	0.19, 0.25, 0.33
H(2)	5.5 (7)	3.3 (6)	4.5 (7)	0.2 (5)	1.6 (6)	−1.1 (5)	0.17, 0.23, 0.29
H(3)	5.6 (7)	3.9 (7)	4.5 (7)	0.5 (6)	0.2 (6)	1.9 (6)	0.17, 0.26, 0.28
H(4)	3.0 (6)	5.7 (8)	5.3 (7)	−1.7 (5)	0.1 (6)	0.7 (6)	0.16, 0.25, 0.29
H(5)	3.6 (6)	5.3 (7)	6.0 (7)	−0.5 (5)	−3.0 (6)	1.0 (6)	0.14, 0.25, 0.33
H(6)	5.2 (7)	5.1 (7)	3.6 (7)	−1.7 (6)	0.5 (5)	1.3 (6)	0.17, 0.24, 0.30
H(7)	2.9 (5)	4.3 (6)	3.6 (6)	1.6 (5)	−1.3 (5)	0.5 (5)	0.11, 0.23, 0.26
H(8)	3.0 (6)	6.5 (8)	3.0 (6)	0.1 (5)	1.3 (5)	0.3 (6)	0.15, 0.23, 0.29
H(10)	3.6 (6)	3.8 (7)	5.2 (7)	−0.2 (5)	−0.6 (5)	0.2 (6)	0.20, 0.22, 0.26
H(11)	3.4 (6)	3.7 (6)	3.5 (6)	−1.4 (5)	0.6 (5)	−0.5 (5)	0.16, 0.20, 0.26
H(12)	2.3 (6)	3.9 (7)	3.1 (6)	0.1 (5)	−1.5 (5)	−1.1 (5)	0.11, 0.20, 0.25
H(13A)	3.0 (7)	5.7 (9)	7.5 (10)	1.4 (7)	−1.8 (7)	−2.2 (7)	0.17, 0.23, 0.35
H(13B)	5.1 (8)	9.3 (11)	2.9 (7)	−1.2 (7)	−0.9 (6)	−1.8 (8)	0.16, 0.26, 0.35
H(13C)	5.7 (9)	8.2 (12)	9.2 (12)	−2.5 (9)	−3.7 (8)	2.9 (10)	0.20, 0.27, 0.42
H(14A)	6.6 (12)	9.3 (14)	13.8 (18)	1.1 (11)	3.9 (12)	−1.2 (13)	0.24, 0.35, 0.44
H(14B)	4.5 (9)	8.5 (12)	11.8 (14)	2.5 (9)	−1.4 (9)	−7.3 (12)	0.16, 0.24, 0.48
H(14C)	7.8 (12)	9.9 (13)	6.1 (10)	5.2 (11)	−1.5 (9)	0.4 (10)	0.19, 0.29, 0.42
			(B) Atoms in Me$_4$N$^+$ Cation				
N	3.65 (4)	4.24 (5)	3.25 (4)	0.31 (4)	−0.23 (4)	−0.16 (4)	0.198, 0.214, 0.237
Me(1)	5.22 (10)	6.58 (12)	4.21 (9)	1.12 (9)	−0.82 (8)	0.77 (8)	0.203, 0.265, 0.302
Me(2)	8.02 (12)	4.30 (9)	3.97 (9)	−0.47 (10)	0.21 (9)	−0.56 (7)	0.212, 0.243, 0.320
Me(3)	6.71 (11)	4.01 (9)	6.28 (12)	−0.46 (9)	−0.93 (10)	0.15 (9)	0.223, 0.263, 0.311
Me (4)	3.58 (9)	11.76 (21)	5.21 (11)	0.97 (11)	−0.45 (8)	−1.33 (13)	0.207, 0.252, 0.392
H(1A)	10.7 (12)	5.9 (10)	4.8 (9)	1.4 (8)	−3.7 (8)	−1.9 (8)	0.18, 0.27, 0.41
H(1B)	6.7 (10)	10.2 (13)	4.4 (9)	5.7 (10)	−2.8 (8)	0.2 (8)	0.10, 0.27, 0.43
H(1C)	9.4 (12)	10.8 (14)	6.5 (11)	−4.1 (10)	−1.8 (8)	4.8 (10)	0.20, 0.29, 0.46
H(2A)	12.7 (13)	4.9 (9)	3.6 (8)	−0.8 (8)	−3.5 (8)	0.6 (7)	0.17, 0.25, 0.42
H(2B)	8.9 (13)	7.0 (11)	7.6 (12)	−0.1 (11)	2.7 (11)	−2.6 (9)	0.23, 0.31, 0.38
H(2C)	17.0 (16)	2.2 (8)	5.2 (9)	−3.5 (9)	−1.0 (9)	1.5 (7)	0.11, 0.26, 0.48
H(3A)	9.9 (12)	5.2 (10)	9.1 (13)	−0.2 (8)	−2.4 (10)	3.4 (9)	0.20, 0.32, 0.41
H(3B)	11.3 (12)	5.2 (9)	5.4 (9)	−0.8 (8)	−2.8 (9)	−3.0 (8)	0.14, 0.31, 0.40
H(3C)	8.5 (12)	5.5 (10)	10.7 (14)	0.0 (10)	3.0 (12)	0.9 (10)	0.26, 0.29, 0.40
H(4A)	1.5 (6)	13.9 (15)	6.6 (10)	0.8 (8)	−1.8 (7)	−1.9 (10)	0.11, 0.29, 0.43
H(4B)	5.6 (9)	13.5 (16)	6.2 (11)	2.4 (9)	−0.1 (8)	−6.5 (11)	0.16, 0.26, 0.47
H(4C)	4.9 (10)	11.1 (15)	9.5 (15)	−2.1 (10)	2.1 (9)	0.9 (12)	0.21, 0.36, 0.39

^{a} These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of A^2. They enter the expression for the structure factor in the form exp[−0.25($B_{11}h^2a^{*2}$ + $B_{22}k^2b^{*2}$ + $B_{33}l^2c^{*2}$ + $2B_{12}hka^*b^*$ + $2B_{13}hla^*c^*$ + $2B_{23}klb^*c^*$)]. ^{b} Esd's were obtained from the last cycle in which thermal parameters *for the atom being considered* were refined. ^{c} These values correspond to the root-mean-square amplitudes of vibration (in A) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

peaks reflect (other) errors in the model (*i.e.*, the use of spherically symmetric scattering factors for all atoms, imprecise treatment of thermal motion, etc.). A third possibility is that these peaks are the result of experimental error in the data systematically adding near the strongest scatterer in the unit cell (as is often observed in structures containing one or a few "heavy" atoms). This third possibility is thought to be improbable, because, while the anion has approximately twice the scattering power of the cation, it is distributed over a correspondingly larger volume.

We are inclined (not without considerable trepidation) toward believing possibility (1), since nearly all the major peaks (14 of the first 18) *are* on the centers of triangular carborane faces and their peak heights are consistent with the C_s symmetry of the anion [*i.e.*, peaks related by this noncrystallographic symmetry are as follows (using the numbering of Table I): peaks 1 and 3; 2 and 5; 6 and 8; 7 (on mirror plane); 10 and 14; 12 (on mirror plane); 13 and 18; 17 (on mirror plane)]. Also, the first peak that is associated with the Me$_4$N$^+$ ion (which has a greater degree of thermal motion than the carborane anion) occurs only after 21 others. However, it is clear

that additional very accurate crystallographic studies of carboranes will be necessary before this suggestion of the detection of bonding electron density can be confirmed unambiguously.

A list of observed and calculated structure factor amplitudes has been deposited.[23]

Positional parameters are shown in Table II; thermal parameters are collected in Table III.

Discussion of the Molecular Structure

Intramolecular distances with their estimated standard deviations (esd's) are given in Table IV; interatomic angles and their esd's are collected in Table V. The overall geometry of the Me$_2$B$_{10}$C$_2$H$_{11}$$^-$ anion is shown in Figures 1 and 2. [These figures show the same view of the anion, but the first illustrates the thermal ellipsoids for boron and carbon atoms and

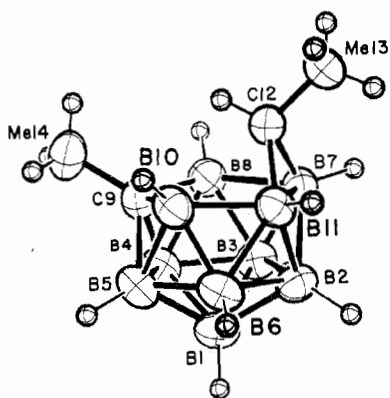(23) See paragraph at end of paper regarding supplementary material.

Figure 1. A general view of the $Me_2B_{10}C_2H_{11}{}^-$ anion, showing the 50% probability contours of the thermal ellipsoids of nonhydrogen atoms. [Hydrogen atoms are shown as artificial spheres of radius 0.10 Å.]

the second shows the thermal ellipsoids of hydrogen atoms.]

The $B_{10}C_2$ cage defines an "opened" icosahedron, with atom B(1) as the "normal" apex, the atoms B(2)-B(3)-B(4)-B(5)-B(6) as the first pentagonal belt, and atoms B(7)-B(8)-C(9)-B(10)-B(11) as the "opened" pentagonal face. The final cage atom, C(12), is bonded directly only to atoms B(7) and B(11) of the icosahedral "cage," with B(7)-C(12) = 1.642 (2) and B(11)-C(12) = 1.641 (2) Å. Distances from C(12) to other cage atoms are C(12)···B(8) = 2.338 (2), C(12)··· B(10) = 2.351 (2), and C(12)···C(9) = 2.816 (2) Å. [We may note that these first two distances, while not within normal bonding range, for which d(C-B) = ~1.70 Å, are, nevertheless, substantially closer than the typical atom–second nearest neighbor distance of ~2.8–2.9 Å within an icosahedral carborane.]

Me(13), the methyl substituent on C(12), is in an exo configuration, while H(12) is in the endo position and is very nearly centered over the open pentagonal face. There are also some close contacts of H(12) with atoms in the carborane cage. These are, in order, H(12)···B(8) = 2.197 (10), H(12)···B(10) = 2.226 (9), H(12)···B(7) = 2.295 (10), H(12)···B(11) = 2.302 (10), and H(12)···C(9) = 2.404 (9) Å.

The open pentagonal face defined by B(7)-B(8)-C(9)-B(10)-B(11) is, in fact, significantly distorted from planarity (see plane II of Table VI), and there is an angle of 9.56° between the plane defined by B(8)-B(7)-B(11)-B(10) [rms deviation from planarity 0.002 Å] and that defined by B(8)-C(9)-B(10).

The "extra" cage atom, C(12), lies slightly over the open pentagonal face as is evidenced by the dihedral angle of 73.82° between plane I (defined by B(7)-C(12)-B(11)) and plane IIA (defined by B(8)-B(7)-B(11)-B(10))—see Table VI. The only other case in which a 12th atom bridges only two atoms of an 11-membered icosahedral fragment is in B_9C_2-$H_{12}AlMe_2$, in which the B-Al-B plane makes an angle of 130.3° with an open pentagonal face of a dicarbollide ligand.[24] [However, it is probable that the aluminum atom is bonded to boron *via* Al-H-B bridges in this molecule.]

Angles around the μ_2-bridging atom C(12) are as follows: B(7)-C(12)-B(11) = 68.3 (1)°; B(7)-C(12)-Me(13) = 113.8 (1)°, B(11)-C(12)-Me(13) = 114.1 (1)°; B(7)-C(12)-H(12) = 121.8 (6)°, B(11)-C(12)-H(12) = 122.6 (6)°; H(12)-C(12)-Me(13) = 110.5 (6)°. Thus, although atom C(12) has a formal coordination number of 4, it clearly is severely distorted from a regular tetrahedral stereochemistry.
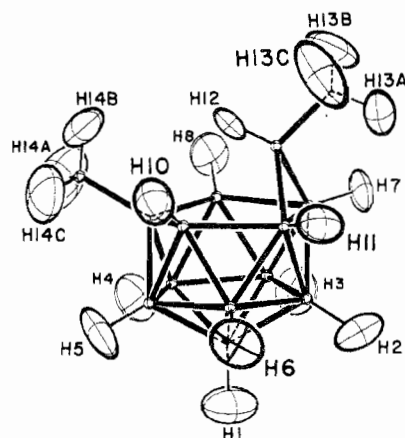
(24) M. R. Churchill and A. H. Reis, *J. Chem. Soc., Dalton Trans.,* 1314 (1972).

Figure 2. The same view of the $Me_2B_{10}C_2H_{11}{}^-$ anion as in Figure 1, now illustrating the 50% probability contours of the thermal ellipsoids of the hydrogen atoms. [Boron and carbon atoms are shown as spheres of radius 0.07 Å.]
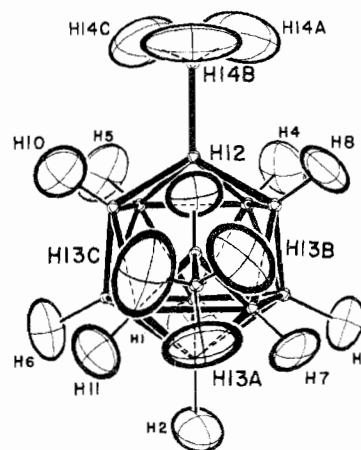

Figure 3. A view demonstrating the approximate C_s symmetry of the $Me_2B_{10}C_2H_{11}{}^-$ anion including the orientation of the thermal ellipsoids of hydrogen atoms. Nonhydrogen atoms are shown as spheres of radius 0.07 Å.

The $Me_2B_{10}C_2H_{11}{}^-$ anion has nearly perfect C_s symmetry. Differences between distances in bond lengths related by the approximate molecular mirror plane are shown in Table IV. The greatest difference in boron–boron bond lengths is 0.008 Å [B(1)-B(3) = 1.792 (2) and B(1)-B(6) = 1.784 (2) Å] and the greatest difference in (cage atom)–hydrogen bond lengths is 0.026 Å [B(4)-H(4) = 1.087 (10) and B(5)-H(5) = 1.113 (10) Å]. We note here that a consideration of deviations from the average of "mirror-related" B-B and B-C distances (for the 12 available pairs) provides an *external* estimate of the standard deviation of distances between nonhydrogen atoms of $[\Sigma(\text{difference}/2)^2/(n-1)]^{1/2} = 0.0022$ Å. This is in excellent agreement with the 0.0019-Å average of values derived from the final least-squares matrix.

The C_s symmetry of the $Me_2B_{10}C_2H_{11}{}^-$ anion extends to the positions of the hydrogen atoms (with slight, but significant, deviations for atoms H(13A), H(13B), and H(13C)) and is even reflected in the orientations of the thermal vibration ellipsoids of hydrogen atoms, including those of the two methyl groups. This is illustrated clearly in Figure 3. Numerical data on the deviations of all atoms from the anion's mirror plane [defined by B(1), B(2), C(9), C(12)] are shown in plane IV of Table VI. The methyl group centered on

Table IV. Intramolecular Distances (in Å) for [Me₄N⁺][Me₂B₁₀C₂H₁₁⁻], with Estimated Standard Deviations[a,b]

Atoms	Dist	Atoms	Dist	Diff
(A) Distances within Me₂B₁₀C₂H₁₁⁻ Anion, Arranged to Show Its C_s Symmetry				
(a) Boron–boron Distances				
B(1)–B(2)	1.757 (2)			
B(1)–B(3)	1.792 (2)	B(1)–B(6)	1.784 (2)	0.008
B(1)–B(4)	1.777 (2)	B(1)–B(5)	1.773 (2)	0.004
B(2)–B(3)	1.799 (2)	B(2)–B(6)	1.793 (2)	0.006
B(2)–B(7)	1.800 (2)	B(2)–B(11)	1.797 (2)	0.003
B(3)–B(4)	1.765 (2)	B(6)–B(5)	1.764 (2)	0.001
B(3)–B(7)	1.796 (2)	B(6)–B(11)	1.792 (2)	0.004
B(3)–B(8)	1.731 (2)	B(6)–B(10)	1.726 (2)	0.005
B(4)–B(5)	1.743 (2)			
B(4)–B(8)	1.800 (2)	B(5)–B(10)	1.794 (2)	0.006
B(7)–B(11)	1.847 (2)			
B(7)–B(8)	1.867 (2)	B(11)–B(10)	1.864 (2)	0.003
(b) Carbon–Boron Distances				
C(9)–B(4)	1.669 (2)	C(9)–B(5)	1.672 (2)	0.003
C(9)–B(8)	1.626 (2)	C(9)–B(10)	1.624 (2)	0.002
C(12)–B(7)	1.642 (2)	C(12)–B(11)	1.641 (2)	0.001
(c) Carbon–Methyl Distances				
C(9)–Me(14)	1.520 (2)			
C(12)–Me(13)	1.518 (2)			
(d) Boron–Hydrogen Distances				
B(1)–H(1)	1.130 (11)			
B(2)–H(2)	1.145 (10)			
B(3)–H(3)	1.133 (11)	B(6)–H(6)	1.130 (11)	0.003
B(4)–H(4)	1.087 (10)	B(5)–H(5)	1.113 (10)	0.026
B(7)–H(7)	1.101 (9)	B(11)–H(11)	1.110 (10)	0.009
B(8)–H(8)	1.101 (10)	B(10)–H(10)	1.106 (11)	0.005
(e) Cage Carbon–Hydrogen Distance				
C(12)–H(12)	0.957 (9)			
(f) Methyl Carbon–Hydrogen Distances				
Me(13)–H(13A)	0.969 (11)	Me(14)–H(14A)	0.983 (16)	
Me(13)–H(13B)	0.995 (11)	Me(14)–H(14B)	0.931 (14)	
Me(13)–H(13C)	0.967 (14)	Me(14)–H(14C)	0.930 (14)	
(B) Distances within Me₄N⁺ Cation				
(a) Nitrogen–Carbon Distances				
N–Me(1)	1.485 (2)	N–Me(3)	1.488 (2)	
N–Me(2)	1.489 (2)	N–Me(4)	1.476 (2)	
(b) Methyl Carbon–Hydrogen Distances				
Me(1)–H(1A)	0.983 (13)	Me(3)–H(3A)	0.979 (15)	
Me(1)–H(1B)	0.922 (13)	Me(3)–H(3B)	0.984 (13)	
Me(1)–H(1C)	1.007 (14)	Me(3)–H(3C)	0.953 (15)	
Me(2)–H(2A)	1.038 (12)	Me(4)–H(4A)	0.956 (15)	
Me(2)–H(2B)	0.934 (14)	Me(4)–H(4B)	0.937 (13)	
Me(2)–H(2C)	0.974 (12)	Me(4)–H(4C)	0.980 (15)	

[a] Esd's are calculated by considering all elements of the positional covariance matrix of the last cycle of refinement. The calculation was performed using the FORTRAN IV program STAN1, by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included. [b] No distances have been corrected for the effects of thermal motion.

Me(13) deviates from the mirror plane by a small rotation about the C(12)–Me(13) bond such that H(13A) lies 0.097 Å from the plane and H(13B) and H(13C) are displaced unsymmetrically from this plane, by +0.736 and −0.831 Å, respectively. However, apart from this one perturbation, the maximum deviation of an atom "on" the mirror plane is 0.014 Å for a hydrogen atom [H(12)] and 0.007 Å for a nonhydrogen atom [Me(14)]. For pairs of atoms disposed about the mirror plane, the largest discrepancies are asymmetries of 0.007 Å for nonhydrogen atoms [atoms B(3) and B(6) are +1.430 and −1.423 Å from the mirror plane] and 0.025 Å for hydrogen atoms [H(4) and H(5) are +1.444 and −1.469 Å from the mirror plane].

Carbon–boron distances fall into three chemically distinct
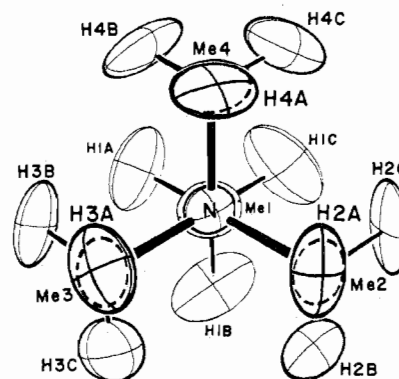
Figure 4. The Me₄N⁺ cation: geometry and 30% probability contours for the thermal ellipsoids of all atoms.

sets: C(9)–B(4) = 1.669 (2) and C(9)–B(5) = 1.672 (2) Å [average 1.671 (2) Å], C(9)–B(8) = 1.626 (2) and C(9)–B(10) = 1.624 (2) Å [average 1.625 (1) Å], and C(12)–B(7) = 1.642 (2) and C(12)–B(11) = 1.641 (2) [average 1.642 (1) Å].

Boron–boron distances vary appreciably and significantly, the shortest being the pair B(3)–B(8) = 1.731 (2) and B(6)–B(10) = 1.726 (2) Å [average 1.729 (4) Å] and the longest being the pair B(7)–B(8) = 1.867 (2) and B(11)–B(10) = 1.864 (2) Å [average 1.866 (2) Å]. The mean of the 21 independent values is 1.788 Å.

The X-ray crystallographically determined boron–hydrogen distances are, of course, a measure of the distance between the centroids of electron density around boron and hydrogen and, as such, are significantly reduced from the true internuclear values. [We may note that the B–H(terminal) bond in diborane is measured as 1.08 (2) Å (average) *via* an X-ray diffraction study,[25] 1.196 (7) Å *via* electron diffraction,[26] and 1.192 (10) Å *via* spectroscopy.[27]]

In the present Me₂B₁₀C₂H₁₁⁻ anion, the 10 individual boron–hydrogen distances range from B(4)–H(4) = 1.087 (10) to B(2)–H(2) = 1.145 (10) Å, with an average value of 1.116 Å (rms scatter 0.018 Å). A careful study of these distances shows that they separate into two sets: (1) B–H bonds adjacent to carbon atoms [*i.e.*, B(4)–H(4), B(5)–H(5); B(7)–H(7), B(11)–H(11); B(8)–H(8), B(10)–H(10)], which average 1.103 Å (rms scatter 0.009 Å; σ(of average) = 0.004 Å);[28] (2) B–H bonds not adjacent to carbon atoms [*i.e.*, B(1)–H(1); B(2)–H(2); B(3)–H(3), B(6)–H(6)] which average 1.135 Å (rms scatter 0.007 Å, σ(of average) = 0.004 Å).[28] While the differences here are small and other systematic effects have been neglected, it is tempting to speculate that the boron atoms furthest from carbon (which have the greatest electron density and are most subject to electrophilic attack[29–34]) may be associated with longer B–H distances (at least, as determined by X-ray diffraction).

(25) D. S. Jones and W. N. Lipscomb, *Acta Crystallogr., Sect. A*, 26, 196 (1970).

(26) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, 42, 1135 (1965).

(27) K. Kuchitscu, *J. Chem. Phys.*, 49, 4456 (1968).

(28) The "root-mean-square scatter" is calculated *via* expression A and the "σ(of average)" *via* expression B. In each expression, x_i is the *i*th value and $\bar{x}$ is the mean of N "equivalent" values.

$$\text{rms} = \left[\sum_{i=1}^{i=N} (x_i - \bar{x})^2 / (N-1) \right]^{1/2} \tag{A}$$

$$\sigma(\text{of average}) = \left[\sum_{i=1}^{i=N} (x_i - \bar{x})^2 / N(N-1) \right]^{1/2} \tag{B}$$

(29) H. Beall and W. N. Lipscomb, *Inorg. Chem.*, 6, 874 (1967).

Table V. Interatomic Angles (in deg) for $[Me_4N^+][Me_2B_{10}C_2H_{11}^-]$

Atoms	Angle	Atoms	Angle	Atoms	Angle	Atoms	Angle
(A) Angles within Triangular Faces of $Me_2B_{10}C_2H_{11}^-$ Anion				**(C) Angles Involving Substituents on Cage**			
B(6)-B(1)-B(2)	60.9 (1)	B(1)-B(6)-B(2)	58.8 (1)	H(1)-B(1)-B(2)	119.8 (6)	H(7)-B(7)-B(2)	113.6 (6)
B(2)-B(1)-B(3)	60.9 (1)	B(2)-B(6)-B(11)	60.2 (1)	H(1)-B(1)-B(3)	123.9 (6)	H(7)-B(7)-B(3)	111.7 (6)
B(3)-B(1)-B(4)	59.3 (1)	B(11)-B(6)-B(10)	64.0 (1)	H(1)-B(1)-B(4)	122.0 (6)	H(7)-B(7)-B(8)	128.8 (6)
B(4)-B(1)-B(5)	58.8 (1)	B(10)-B(6)-B(5)	61.9 (1)	H(1)-B(1)-B(5)	121.3 (7)	H(7)-B(7)-C(12)	112.0 (6)
B(5)-B(1)-B(6)	59.5 (1)	B(5)-B(6)-B(1)	60.0 (1)	H(1)-B(1)-B(6)	122.9 (6)	H(7)-B(7)-B(11)	128.2 (6)
B(1)-B(2)-B(3)	60.5 (1)	B(8)-B(7)-B(3)	56.4 (1)	H(2)-B(2)-B(1)	118.1 (6)	H(8)-B(8)-B(7)	116.8 (6)
B(3)-B(2)-B(7)	59.9 (1)	B(3)-B(7)-B(2)	60.0 (1)	H(2)-B(2)-B(3)	122.8 (6)	H(8)-B(8)-B(3)	126.6 (6)
B(7)-B(2)-B(11)	61.7 (1)	B(2)-B(7)-B(11)	59.1 (1)	H(2)-B(2)-B(7)	120.6 (6)	H(8)-B(8)-B(4)	124.2 (6)
B(11)-B(2)-B(6)	59.9 (1)	B(11)-B(7)-C(12)	55.8 (1)	H(2)-B(2)-B(11)	121.1 (6)	H(8)-B(8)-C(9)	119.0 (6)
B(6)-B(2)-B(1)	60.3 (1)	B(7)-B(8)-B(3)	59.8 (1)	H(2)-B(2)-B(6)	123.2 (6)	Me(14)-C(9)-B(8)	117.8 (1)
B(1)-B(3)-B(2)	58.6 (1)	B(3)-B(8)-B(4)	60.0 (1)	H(3)-B(3)-B(1)	122.4 (6)	Me(14)-C(9)-B(4)	120.3 (1)
B(2)-B(3)-B(7)	60.1 (1)	B(4)-B(8)-C(9)	58.1 (1)	H(3)-B(3)-B(2)	120.3 (6)	Me(14)-C(9)-B(5)	120.7 (1)
B(7)-B(3)-B(8)	63.9 (1)	B(8)-C(9)-B(4)	66.2 (1)	H(3)-B(3)-B(7)	115.2 (6)	Me(14)-C(9)-B(10)	118.4 (1)
B(8)-B(3)-B(4)	62.0 (1)	B(4)-C(9)-B(5)	62.9 (1)	H(3)-B(3)-B(8)	123.6 (6)	H(10)-B(10)-C(9)	118.3 (6)
B(4)-B(3)-B(2)	60.0 (1)	B(5)-C(9)-B(10)	65.9 (1)	H(3)-B(3)-B(4)	121.3 (6)	H(10)-B(10)-B(5)	123.1 (6)
B(1)-B(4)-B(3)	60.8 (1)	C(9)-B(10)-B(5)	58.3 (1)	H(4)-B(4)-B(1)	127.9 (6)	H(10)-B(10)-B(6)	126.8 (6)
B(3)-B(4)-B(8)	58.1 (1)	B(5)-B(10)-B(6)	60.1 (1)	H(4)-B(4)-B(3)	125.5 (6)	H(10)-B(10)-B(11)	118.0 (5)
B(8)-B(4)-C(9)	55.7 (1)	B(6)-B(10)-B(11)	59.8 (1)	H(4)-B(4)-B(8)	121.7 (6)	H(11)-B(11)-B(10)	128.5 (6)
C(9)-B(4)-B(5)	58.6 (1)	B(10)-B(11)-B(6)	56.3 (1)	H(4)-B(4)-C(9)	120.0 (6)	H(11)-B(11)-B(6)	112.8 (5)
B(5)-B(4)-B(1)	60.5 (1)	B(6)-B(11)-B(2)	60.0 (1)	H(4)-B(4)-B(5)	121.6 (6)	H(11)-B(11)-B(2)	114.4 (5)
B(1)-B(5)-B(4)	60.7 (1)	B(2)-B(11)-B(7)	59.3 (1)	H(5)-B(5)-B(1)	124.9 (6)	H(11)-B(11)-B(7)	127.2 (6)
B(4)-B(5)-C(9)	58.5 (1)	B(7)-B(11)-C(12)	55.9 (1)	H(5)-B(5)-B(4)	122.7 (6)	H(11)-B(11)-C(12)	110.4 (5)
C(9)-B(5)-B(10)	55.7 (1)	B(11)-C(12)-B(7)	68.3 (1)	H(5)-B(5)-C(9)	123.5 (7)	H(12)-C(12)-B(7)	121.8 (6)
B(10)-B(5)-B(6)	58.0 (1)			H(5)-B(5)-B(10)	123.2 (6)	H(12)-C(12)-B(11)	122.6 (6)
B(6)-B(5)-B(1)	60.6 (1)			H(5)-B(5)-B(6)	123.2 (7)	H(12)-C(12)-Me(13)	110.5 (6)
				H(6)-B(6)-B(1)	122.7 (6)	Me(13)-C(12)-B(7)	113.8 (1)
(B) Angles within Pentagonal Rings of $Me_2B_{10}C_2H_{11}^-$ Anion				H(6)-B(6)-B(5)	123.0 (6)	Me(13)-C(12)-B(11)	114.1 (1)
B(2)-B(1)-B(4)	110.0 (1)	B(1)-B(6)-B(10)	107.2 (1)	H(6)-B(6)-B(10)	124.0 (6)		
B(3)-B(1)-B(5)	105.9 (1)	B(5)-B(6)-B(11)	116.3 (1)	H(6)-B(6)-B(11)	113.8 (6)		
B(4)-B(1)-B(6)	105.9 (1)	B(10)-B(6)-B(2)	107.6 (1)	H(6)-B(6)-B(2)	118.5 (6)		
B(5)-B(1)-B(2)	110.1 (1)	B(11)-B(6)-B(1)	110.3 (1)				
B(6)-B(1)-B(3)	105.9 (1)	B(2)-B(6)-B(5)	108.9 (1)	**(D) Angles within Cage Methyl Groups**			
B(1)-B(2)-B(7)	111.6 (1)	B(2)-B(7)-C(12)	114.3 (1)	H(13A)-Me(13)-C(12)	112.0 (7)	H(13A)-Me(13)-H(13B)	108.6 (11)
B(3)-B(2)-B(11)	108.1 (1)	B(11)-B(7)-B(8)	101.4 (1)	H(13B)-Me(13)-C(12)	110.9 (7)	H(13B)-Me(13)-H(13C)	107.7 (12)
B(7)-B(2)-B(6)	108.4 (1)	C(12)-B(7)-B(3)	133.2 (1)	H(13C)-Me(13)-C(12)	111.9 (8)	H(13C)-Me(13)-H(13A)	105.5 (11)
B(11)-B(2)-B(1)	111.3 (1)	B(8)-B(7)-B(2)	101.6 (1)	H(14A)-Me(14)-C(9)	112.4 (9)	H(14A)-Me(14)-H(14B)	107.2 (13)
B(6)-B(2)-B(3)	105.2 (1)	B(3)-B(7)-B(11)	106.2 (1)	H(14B)-Me(14)-C(9)	113.5 (8)	H(14B)-Me(14)-H(14C)	104.4 (13)
B(1)-B(3)-B(7)	110.1 (1)	B(8)-B(7)-C(12)	83.3 (1)	H(14C)-Me(14)-C(9)	109.8 (9)	H(14C)-Me(14)-H(14A)	109.3 (12)
B(2)-B(3)-B(8)	107.2 (1)	B(3)-B(8)-C(9)	106.5 (1)				
B(7)-B(3)-B(4)	116.4 (1)	B(7)-B(8)-B(4)	111.2 (1)	**(E) Angles within Me_4N^+ Cation**			
B(8)-B(3)-B(1)	107.1 (1)	C(9)-B(8)-B(7)	114.6 (1)	Me(1)-N-Me(2)	109.7 (1)	Me(2)-N-Me(3)	109.0 (1)
B(4)-B(3)-B(2)	108.6 (1)	B(4)-C(9)-B(10)	115.5 (1)	Me(1)-N-Me(3)	109.4 (1)	Me(2)-N-Me(4)	109.5 (1)
B(1)-B(4)-B(8)	104.8 (1)	B(10)-C(9)-B(8)	106.7 (1)	Me(1)-N-Me(4)	109.6 (1)	Me(3)-N-Me(4)	109.8 (1)
B(3)-B(4)-C(9)	103.1 (1)	B(8)-C(9)-B(5)	115.6 (1)	H(1A)-Me(1)-N	106.3 (8)	H(1A)-Me(1)-H(1B)	113.0 (12)
B(8)-B(4)-B(5)	103.9 (1)	C(9)-B(10)-B(11)	114.2 (1)	H(1B)-Me(1)-N	107.8 (8)	H(1B)-Me(1)-H(1C)	111.2 (13)
C(9)-B(4)-B(1)	104.6 (1)	B(11)-B(10)-B(5)	111.3 (1)	H(1C)-Me(1)-N	107.4 (8)	H(1C)-Me(1)-H(1A)	110.9 (12)
B(5)-B(4)-B(3)	108.4 (1)	B(6)-B(10)-C(9)	106.7 (1)	H(2A)-Me(2)-N	108.4 (7)	H(2A)-Me(1)-H(2B)	109.9 (12)
B(1)-B(5)-C(9)	104.6 (1)	B(10)-B(11)-C(12)	84.0 (1)	H(2B)-Me(2)-N	105.7 (9)	H(2B)-Me(1)-H(2C)	117.0 (12)
B(4)-B(5)-B(10)	103.9 (1)	C(12)-B(11)-B(2)	114.5 (1)	H(2C)-Me(2)-N	107.6 (8)	H(2C)-Me(1)-H(2A)	107.9 (11)
C(9)-B(5)-B(6)	102.9 (1)	B(7)-B(11)-B(6)	106.5 (1)	H(3A)-Me(3)-N	108.4 (8)	H(3A)-Me(3)-H(3B)	108.9 (11)
B(10)-B(5)-B(1)	104.8 (1)	B(2)-B(11)-B(10)	101.7 (1)	H(3B)-Me(3)-N	103.3 (8)	H(3B)-Me(3)-H(3C)	117.3 (13)
B(6)-B(5)-B(4)	108.3 (1)	B(10)-B(11)-B(7)	102.2 (1)	H(3C)-Me(3)-N	103.2 (9)	H(3C)-Me(3)-H(3A)	114.8 (14)
				H(4A)-Me(4)-N	106.6 (8)	H(4A)-Me(4)-H(4B)	113.0 (14)
				H(4B)-Me(4)-N	108.0 (9)	H(4B)-Me(4)-H(4C)	112.1 (13)
				H(4C)-Me(4)-N	109.2 (9)	H(4C)-Me(4)-H(4A)	107.7 (12)

The carbon-hydrogen distance in the icosahedral cage is C(12)-H(12) = 0.957 (9) Å and carbon-methyl distances are C(9)-Me(14) = 1.520 (2) and C(12)-Me(13) = 1.518 (2) Å. Within the C-bonded methyl groups, distances range from Me(14)-H(14C) = 0.930 (14) to Me(13)-H(13B) = 0.995 (11) Å, with a mean value of 0.963 Å (rms scatter 0.027 Å, σ(of average) = 0.011 Å). [Again, these values

are between centroids of electron density and systematically shorter than the true internuclear distance of ~1.08 Å.[35]]

The C-Me-H angles range from 109.8 (9) to 113.5 (8)°, while H-Me-H angles range from 104.4 (13) to 109.3 (12)°.

The Tetramethylammonium Cation

The Me_4N^+ cation, viewed down one of its C_3 axes, is shown in Figure 4. Once again, the vibration ellipsoids of the hydrogen atoms look meaningful (*i.e.*, are suggestive of librational motion about the four N-C bonds), thereby justifying our use of anisotropic thermal parameters for these atoms.

The nitrogen-carbon distances range from N-Me(4) = 1.476 (2) to N-Me(2) = 1.489 (2) Å, averaging 1.485 Å (rms scat-

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Table VI. Least-Squares Planes and Dihedral Angles in the Me$_2$B$_{10}$C$_2$H$_{11}^-$ Anion^{a-c}

Distances of Atoms from Planes, Å

Plane I: $0.9833X - 0.0529Y + 0.1743Z = 2.057$

C(12)*	0.000		
B(7)*	0.000	B(11)*	0.000

Plane II: $-0.1715X - 0.7493Y - 0.6396Z = -5.302$

C(9)*	-0.070		
B(7)*	-0.021	B(11)*	-0.016
B(8)*	0.055	B(10)*	0.052
C(12)	1.300		
H(12)	1.722		
Me(14)	0.704		
H(7)	0.150	H(11)	0.186
H(8)	0.706	H(10)	0.697

Plane IIA: $-0.2096X - 0.7392Y - 0.6400Z = -5.348$

B(7)*	-0.002	B(11)*	0.002
B(8)*	0.001	B(10)*	-0.001
C(9)	-0.161		

Plane IIB: $-0.0470X - 0.7747Y - 0.6306Z = -4.875$

C(9)*	0.000		
B(8)*	0.000	B(10)*	0.000
B(7)	-0.307	B(11)	-0.300

Plane III: $-0.1826X - 0.7457Y - 0.6408Z = -6.808$

B(2)*	-0.056		
B(3)*	0.046	B(6)*	0.047
B(4)*	-0.017	B(5)*	-0.019
H(2)	-0.658		
H(3)	-0.418	H(6)	-0.406
H(4)	-0.403	H(5)	-0.469
B(1)	-0.940		

Plane IV: $0.1747X + 0.6185Y - 0.7661Z = 2.271$

B(1)*	0.000		
B(2)*	-0.000		
C(9)*	-0.000		
C(12)*	0.000		
Me(14)	0.007		
Me(13)	0.000		
B(3)	1.430	B(6)	-1.423
B(4)	0.873	B(5)	-0.870
B(7)	0.922	B(11)	-0.920
B(8)	1.301	B(10)	-1.305
H(12)	0.014		
H(1)	-0.010		
H(2)	0.003		
H(13A)	0.097		
H(13B)	0.736	H(13C)	-0.831
H(14B)	-0.003		
H(14A)	0.788	H(14C)	-0.770
H(3)	2.417	H(6)	-2.398
H(4)	1.444	H(5)	-1.469
H(7)	1.598	H(11)	-1.597
H(8)	2.132	H(10)	-2.142

Dihedral Angles, Deg

I–II	76.08	I–IV	90.31
I–IIA	73.82	II–IV	90.19
IIA–IIB	9.56	IIA–IV	90.20
II–IIA	2.26	IIB–IV	90.24
II–IIB	7.31	III–IV	90.12
II–III	0.67		

^{a} Equations for planes are in cartesian coordinates such that $X = xa + zc \cos \beta$, $Y = yb$, and $Z = zc \sin \beta$. ^{b} Planes are derived using unit weights for atoms marked with an asterisk and zero weight for all other atoms. ^{c} Entries are arranged so as to illustrate the (noncrystallographic) C_s symmetry of the anion.

ter 0.006 Å). Within the methyl groups, carbon–hydrogen distances range from 0.922 (13) to 1.038 (12) Å, averaging 0.971 Å (rms scatter 0.033 Å). The N–Me–H angles range from 103.2 (9) to 109.2 (9)°, while H–Me–H angles vary from 107.7 (12) to 117.3 (13)°.

Interionic Contacts

Interionic H···H distances are listed in Table VII. The

Table VII. Interionic H···H Distances^a in the [Me$_4$N$^+$][Me$_2$B$_{10}$C$_2$H$_{11}^-$] Crystal

Atoms	Dist, Å	Symmetry transformation of 2nd atom
I. Cation–Cation (to 3.5 Å)		
H(1C)···H(2A)	3.23 (2)	$c + (0, 0, 0)$
H(1C)···H(2B)	3.28 (2)	$c + (0, 0, 0)$
H(1C)···H(2C)	3.48 (2)	$c + (0, 0, 0)$
II. Anion–Anion (to 3.0 Å)		
H(7)···H(13A)	2.52 (2)	$\bar{1} + (0, 1, 0)$
H(11)···H(13B)	2.54 (2)	$c + (0, 0, 0)$
H(4)···H(8)	2.65 (1)	$\bar{1} + (1, 1, 0)$
H(5)···H(14B)	2.72 (2)	$c + (0, 0, 0)$
H(6)···H(12)	2.80 (1)	$c + (0, 0, 0)$
H(6)···H(13C)	2.83 (2)	$c + (0, 0, 0)$
H(6)···H(13B)	2.87 (2)	$c + (0, 0, 0)$
H(1)···H(14C)	2.90 (2)	$2_1 + (1, 0, 0)$
III. Anion–Cation (to 3.0 Å)		
H(3)···H(1C)	2.31 (2)	$2_1 + (1, 0, 0)$
H(6)···H(1A)	2.38 (2)	$\bar{1} + (1, 1, 1)$
H(11)···H(1B)	2.45 (2)	$1 + (-1, 0, 0)$
H(10)···H(3A)	2.48 (2)	$2_1 + (1, -1, 0)$
H(13A)···H(2B)	2.50 (2)	$1 + (-1, 0, 0)$
H(1)···H(2C)	2.51 (2)	$2_1 + (1, 0, 0)$
H(6)···H(4B)	2.51 (2)	$\bar{1} + (1, 1, 1)$
H(4)···H(4A)	2.52 (2)	$1 + (0, 0, 0)$
H(3)···H(2A)	2.54 (2)	$\bar{1} + (1, 1, 0)$
H(3)···H(2C)	2.54 (2)	$2_1 + (1, 0, 0)$
H(13C)···H(1B)	2.58 (2)	$c + (-1, 0, -1)$
H(13C)···H(3B)	2.61 (2)	$2_1 + (1, 1, 1)$
H(6)···H(3B)	2.63 (2)	$\bar{1} + (1, 1, 1)$
H(8)···H(3A)	2.63 (2)	$\bar{1} + (1, 1, 0)$
H(5)···H(4C)	2.64 (2)	$1 + (0, 0, 0)$
H(2)···H(3C)	2.65 (2)	$1 + (-1, 0, 0)$
H(8)···H(2A)	2.72 (2)	$\bar{1} + (1, 1, 0)$
H(13B)···H(3A)	2.72 (2)	$\bar{1} + (1, 1, 0)$
H(7)···H(2A)	2.75 (2)	$\bar{1} + (1, 1, 0)$
H(11)···H(2B)	2.75 (2)	$1 + (-1, 0, 0)$
H(2)···H(1A)	2.76 (2)	$\bar{1} + (1, 1, 1)$
H(13B)···H(1B)	2.76 (2)	$c + (-1, 0, -1)$
H(10)···H(3B)	2.78 (2)	$2_1 + (1, -1, 0)$
H(11)···H(3C)	2.78 (2)	$1 + (-1, 0, 0)$
H(8)···H(4A)	2.80 (2)	$\bar{1} + (1, 1, 0)$
H(7)···H(3A)	2.84 (2)	$\bar{1} + (1, 1, 0)$
H(1)···H(4B)	2.86 (2)	$\bar{1} + (1, 1, 1)$
H(14A)···H(2A)	2.92 (2)	$1 + (0, 0, 0)$
H(1)···H(1A)	2.94 (2)	$\bar{1} + (1, 1, 1)$
H(2)···H(2C)	2.94 (2)	$2_1 + (1, 0, 0)$
H(3)···H(4C)	2.96 (2)	$2_1 + (1, 0, 0)$
H(7)···H(2B)	2.99 (2)	$\bar{1} + (1, 1, 0)$

^{a} The apparent shortening of the B–H and C–H bonds characteristic of X-ray diffraction studies (see text and ref 35) will cause the corresponding *internuclear* H···H distances to be *less* than the values listed here by as much as 0.2 Å.

shortest of these (2.31 (2) Å for H(3)···H(1C); 2.38 (2) Å for H(6)···H(1A); etc.) are somewhat less than the accepted 2.4-Å value for hydrogen van der Waals distances[36] but do not seem to have had any appreciable effect on the ions' conformations. Some or all of the reason for this might be found in the substantial increase in distance upon correcting for the atoms' "independent" thermal motions (*i.e.*, the time-average of instantaneous separations is greater than the separation of the average positions). Busing and Levy[37] have given a quantitative treatment of this effect.

(36) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(37) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 17, 142 (1964).

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edi-

tion 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-73-2674.

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Synthesis, Characterization, and Aquation Kinetics of Thiolatobis(ethylenediamine)chromium(III) Complexes

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A general procedure for the synthesis of thiolatobis(ethylenediamine)chromium(III) complexes has been developed. These compounds exhibit an intense absorption in the near-ultraviolet spectrum which is characteristic of metal–sulfur bonding. The rates of aquation of two specific complexes, [Cr(en)$_2$(SCH$_2$COO)]$^+$ and [Cr(en)$_2$(SCH$_2$CH$_2$NH$_2$)]$^{2+}$, in aqueous perchloric acid media are reported as a function of acid concentration, ionic strength, and temperature. Aquation of both complexes is formulated as an approach to equilibrium between chelated and monodentate thiolato ligands, equilibrium being attained *via* the making and breaking of Cr–S bonds. This reaction proceeds predominantly through acid-catalyzed Cr–S bond fission, although the rates of acid-independent Cr–S and Cr–N bond cleavage are also competitive. The rates of Cr–S bond breaking are at least 10^4 times greater than the rates of Co–S bond breaking in the analogous cobalt(III) compounds [Co(en)$_2$(SCH$_2$COO)]$^+$ and [Co(en)$_2$(SCH$_2$CH$_2$NH$_2$)]$^{2+}$. This effect is in part attributed to the different Bronsted basicities of thiolato sulfur coordinated to cobalt(III) and chromium(III).

Introduction

Recent reports[1,2] that low-valent sulfur functions as a remarkably efficient bridge for electron transfer from chromium(II) to cobalt(III) have generated considerable interest in the chemistry of thiolato complexes of cobalt(III) and chromium(III).[3,4] In order to investigate the efficiency of electron transfer through a thiolato bridge to chromium(III), we have prepared certain thiolatobis(ethylenediammine)chromium(III) complexes by the reduction of organic disulfides with ethylenediamine–chromium(II) mixtures. Since these are the first examples of thiolatoamminechromium(III) compounds and because Cr^{III}–S bonds are well known to be more labile than Co^{III}–S bonds,[5] we felt it necessary to investigate thoroughly the thermal aquation of two specific complexes, [Cr(en)$_2$(SCH$_2$COO)]$^+$ and [Cr(en)$_2$(SCH$_2$CH$_2$NH$_2$)]$^{2+}$, before commencing redox studies. These investigations have not only aided in characterizing this new class of complexes but, since detailed kinetic studies of metal–sulfur bond cleavage are relatively rare,[3] they have also significantly extended the range of experimental results pertaining to ligand substitution reactions. Therefore in this paper we report on acid-catalyzed Cr–S bond fission, which for the above two complexes is generally faster than, but competitive with, acid-independent Cr–S and Cr–N bond fission. Cleavage of the Cr–S linkage in these complexes may be generally classified as an acid-catalyzed replacement of a basic multidentate ligand; evidence is also presented for the reverse of this reac-

tion *via* Cr–S bond formation. The corresponding cobalt-(III) complexes, [Co(en)$_2$(SCH$_2$COO)]$^+$ and [Co(en)$_2$(SCH$_2$·CH$_2$NH$_2$)]$^{2+}$, are shown to be completely inert to Co–S bond fission under the conditions employed in this study.

Experimental Section

Equipment. Visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer at room temperature, infrared spectra were recorded on a Beckman IR-10 spectrophotometer, and molecular weights were obtained with a Model 115 Hitachi Perkin-Elmer molecular weight apparatus. Kinetic experiments were followed on a Cary Model 16K spectrophotometer equipped with a thermostated cell compartment that maintained the temperature of reacting solutions to better than ±0.2°. Computer calculations were performed on an IBM System 360 located at the University of Chicago Computation Center. The standard Los Alamos nonlinear least-squares program was adapted to this system and used for all data analyses.[6]

Materials. All common laboratory chemicals were of reagent grade. Water was distilled two times in Pyrex equipment. G. Frederick Smith doubly distilled perchloric acid was used for all kinetic experiments. Dowex 50W-X2 ion-exchange resin, 200–400 mesh, was kindly donated by Dow Chemical Co. and was cleaned by a previously outlined procedure.[7] **Cystamine dihydrochloride** (97%) and **dithiodiglycolic acid** (96%) were obtained from Aldrich Chemical Co. and were used in preparative procedures without further purification. Chromium metal (99.999%) was purchased from Apache Chemicals. Salts of *O,S*-mercaptoacetatobis(ethylenediamine)cobalt-(III) and *N,S*-(2-mercaptoethylamine)bis(ethylenediamine)cobalt(III)[8] were prepared by the method of Lane and Bennett[1] and were recrystallized three times before use.

Analyses. Elemental analyses of solid compounds were performed by PCR Inc. of Gainesville, Fla. Molecular weights were

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