TABLE VIII
ANGLE SUMMARY[a]

		Deg			
Angle	Symmetry-related angles	Mean value	Av dev	Max dev	Std dev of mean
2–1–Cl	3–1–Cl, 4–1–Cl, 5–1–Cl	129.2	2.5	6.6	1.4
2–6–Cl	3–6–Cl, 4–8–Cl, 5–8–Cl	114.8	2.5	9.3	1.5
7–6–Cl	9–6–Cl, 7–8–Cl, 9–8–Cl	130.9	3.8	8.9	1.9
10–6–Cl	10–8–Cl	121.9	1.9	2.2	1.3
6–10–7	7–10–8, 8–10–9, 9–10–6	66.1	2.7	5.6	1.3
2–1–3	4–1–5	65.9	2.1	2.8	1.5
2–1–5	3–1–4	66.7	0.9	1.6	0.7
2–3–4	3–4–5, 4–5–2, 5–2–3	90.0	2.2	5.4	1.1
7–6–9	7–8–9	93.8	2.7	4.5	2.0
8–7–6	6–9–8	86.1	3.3	6.5	2.7
4–3–7	3–4–7, 2–5–9, 5–2–9	58.5	1.0	3.1	0.5
2–3–6	3–2–6, 4–5–8, 5–4–8	59.0	3.0	4.3	1.3
3–6–7	2–6–9, 4–8–7, 5–8–9	59.2	1.5	3.5	0.7
3–7–6	4–7–8, 2–9–6, 5–9–8	59.2	1.9	5.3	1.0
9–2–6	6–3–7, 7–4–8, 8–5–9	61.7	1.5	4.0	0.8
2–6–3	4–8–5	62.1	1.5	2.9	1.1
3–7–4	2–9–5	63.0	1.2	2.5	1.1
C–N–C	6 equiv bonds				
	Molecule 1	109.4	2.9	6.8	1.7
	Molecule 2	109.5	1.2	2.7	0.7
	Molecule 3	107.5	12.6	30.0	8.0
	Molecule 4	109.4	3.1	6.3	1.7

[a] The average deviation of all angles (comparing symmetry-related bonds in both molecules) is 3.0°. The average deviation if the disordered tetramethylammonium is not considered is 2.2°. The average deviation of B–B–Cl angles is 2.8°; B–B–B angles, 2.0°; C–N–C angles, 4.9°; C–N–C angles if the disorder is not considered, 2.4°.

substitution here. Studies of other substituted products are desirable in order further to elucidate this sequence. The Cl atom at only one apex does indeed agree with the results of the nmr study,[3] which did not yield the positions for the other two Cl atoms of this $B_{10}H_7Cl_3^{2-}$ ion.

Comparison of the present $B_{10}H_7Cl_3^{2-}$ ion with structures for $Cu_2B_{10}H_{10}$,[19] the photoisomer of $B_{20}H_{18}^{2-}$,[20] the "normal" isomer of $B_{20}H_{18}^{2-}$,[21] and $B_{20}H_{17}NO^{3-}$ [22] indicates that the B_{10} units in these species are very similar within the large standard deviations of all of these studies. Average distances are as follows: apex to edge: 1.69, 1.73, 1.68, 1.70, and 1.72 Å; edge to edge in the square pyramid: 1.85, 1.86, 1.83, 1.84, and 1.87 Å; edge to edge in the equatorial belt: 1.79, 1.82, 1.79, 1.81, and 1.82 Å in the B_{10} units of these species in the order listed. Of course, these averages ignore distortions which arise from the strong bonding interactions in the local environments of the B_{10} units. What is probably noteworthy is that fairly consistent *average* distances do occur in spite of these different environments. Moreover, the detailed distortions of chemical bonding of these B_{10} units appear to be fairly small but will have to await X-ray studies at higher precision than those available so far.

Acknowledgment.—We wish to thank A. Kaczmarczyk for the sample and for informing us of the nmr results, and we acknowledge support by the Office of Naval Research.

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The Molecular and Crystal Structure of Ethylenediamine–Bisborane, $C_2H_{14}B_2N_2$

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In the solid state ethylenediamine–bisborane is an open-chain molecule which exists in the trans conformation. The molecule contains a center of symmetry and all nonhydrogen atoms lie within 0.005 Å of a least-squares fitted plane. The compound crystallizes in the space group *Pbca* and the cell dimensions are $a = 10.761$ (3) Å, $b = 8.172$ (8) Å, and $c = 8.131$ (14) Å. The observed and calculated densities are 0.83 and 0.82 g cm^{-3}, respectively. The intensities were collected by counter techniques and the model was refined to a conventional R factor of 0.062. The C–C distance is 1.514 (7) Å, the C–N distance is 1.477 (5) Å, and the N–B distance is 1.600 (7) Å. The molecule essentially has C_{2h} symmetry in the solid state.

Introduction

Ethylenediamine–bisborane has been shown to be a neutral monomer with a BH_3 group coordinated to each nitrogen atom of the diamine in an open-chain configuration.[1] In a previous study, the infrared spectrum of ethylenediamine–bisborane was compared with the spectra of selected ethylenediamine–metal complexes.[2] The gauche conformation was assigned to the ethylenediamine residue, and a cyclic structure was proposed. Although the molecule has been shown to be an open-chain configuration, the question remained whether ethylenediamine–bisborane exists in a gauche or trans conformation in the solid state. The present study was undertaken to resolve this question.

Experimental Section

Ethylenediamine–bisborane was synthesized[1] and the crystalline product recrystallized from distilled water. A single crystal with dimensions of 0.72 × 0.36 × 0.30 mm was chosen for study, and the crystal was mounted with the long edge (c axis) coincident with the rotation axis. Precession and Weissenberg photographs, calibrated with superimposed NaCl powder lines ($a = 5.6402$ Å), were used to determine the unit cell dimensions and space group. The errors in cell edges are the average deviations calculated from measurements of several higher angle reflections or layer lines. The density was determined by the flotation technique using a mixture of toluene and 1-hexene.

Crystal Data

$C_2H_{14}B_2N_2$, mol wt 87.77, has unit cell dimensions $a = 10.761$ (3) Å, $b = 8.172$ (8) Å, $c = 8.131$ (14) Å; systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$; space group *Pbca* (D_{2h}^{15}, no. 61); $Z = 4$; $V = 715$ Å^3; $\mu = 0.51$ cm^{-1} (Mo Kα); $d_{\text{obsd}} = 0.83$ g cm^{-3}; $d_{\text{calcd}} = 0.82$ g cm^{-3}; λ (Cr Kα) 2.2909 Å.

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(2) J. Goubeau and H. Schneider, *Ber.*, **94**, 816 (1961).

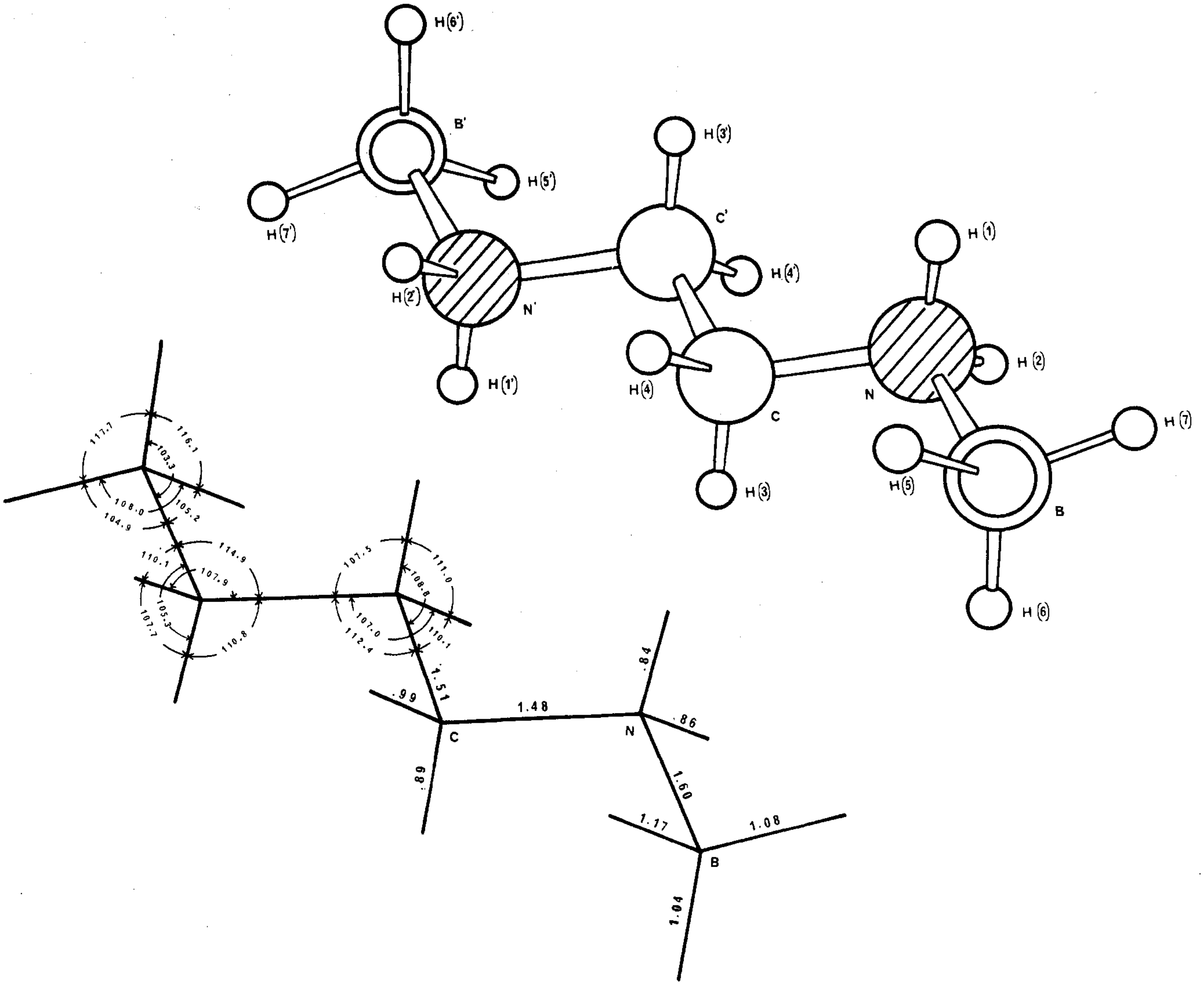

Figure 1.—Molecular structure of ethylenediamine–bisborane.

Three-dimensional intensity data were collected through the sixth level (*hk*0–*hk*6) with a Philips PAILRED diffractometer using equiinclination geometry and a continuous ω-scan technique. Mo Kα radiation (λ 0.71069 Å) and a silicon monochromator crystal [*d*(111) = 3.1355 Å] were used. A 2° ω-scan range and a scan speed of 0.5°/min were selected. One-minute background counts were taken on either side of the scan range. A total of 1081 reflections were recorded which corresponds to approximately 80% of the reflections within the region (sin θ)/λ < 0.62. Several reference reflections were monitored during data collection and changes in intensities were less than 5%.

Lorentz and polarization corrections were applied to the data, but no corrections for absorption were made. Reflections of the type *hkl* and $\bar{h}kl$ were averaged and a total of 331 independent observed reflections ($\sigma(F_o) < {}^1/_2 F_o$) were obtained. Standard deviations were assigned on the basis of counting statistics.[3] The intensities of the reference reflections were used to scale the levels together initially. Level scaling was checked at several points during the model refinement.

Structure Determination and Model Refinement

A three-dimensional Patterson map was calculated with the origin peak removed. The superposition method was used to extract the molecular arrangement. The molecule contains a center of symmetry and the atomic coordinates of one nitrogen, one carbon, and one boron atom were used in two cycles of isotropic full-matrix least-squares refinement. The *R* factor for 331 observed reflections was 0.119 where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. Atomic scattering factors of neutral nitrogen, carbon, and boron were taken from ref 4. Three additional cycles of isotropic refinement dropped *R* to 0.09 and R_w to 0.076 where $R_w = \Sigma w||F_o| - |F_c||/\Sigma w|F_o|$. The weighting scheme used in the refinement was $w = 1/\sigma(F_o)^2$.

Hydrogen atom positions were obtained from a difference Fourier map. Six cycles of least-squares refinement with all nonhydrogen atoms assigned anisotropic temperature factors gave $R = 0.062$ and $R_w = 0.051$. The atomic scattering factors of Stewart, Davidson, and Simpson were used for hydrogen.[5]

Final positional and thermal parameters, along with their estimated standard deviations, are given in Table I.[6] The estimated standard deviations of the parameters were obtained from the inverse of the normal-equations matrix of the last least-squares cycle. All shifts of the parameters during the final cycle of full-matrix refinement were less than one-third of the estimated standard deviation of the parameter. A final three-dimensional difference Fourier map was calculated and the largest peak was 0.12 e/Å^3. A listing of interatomic distances is given in Table II.

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(3) D. R. Johnson and W. H. Watson, *Inorg. Chem.*, **10**, 1068 (1971).

(4) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 201.

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(6) A listing of the squares of the observed and calculated structure factors will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

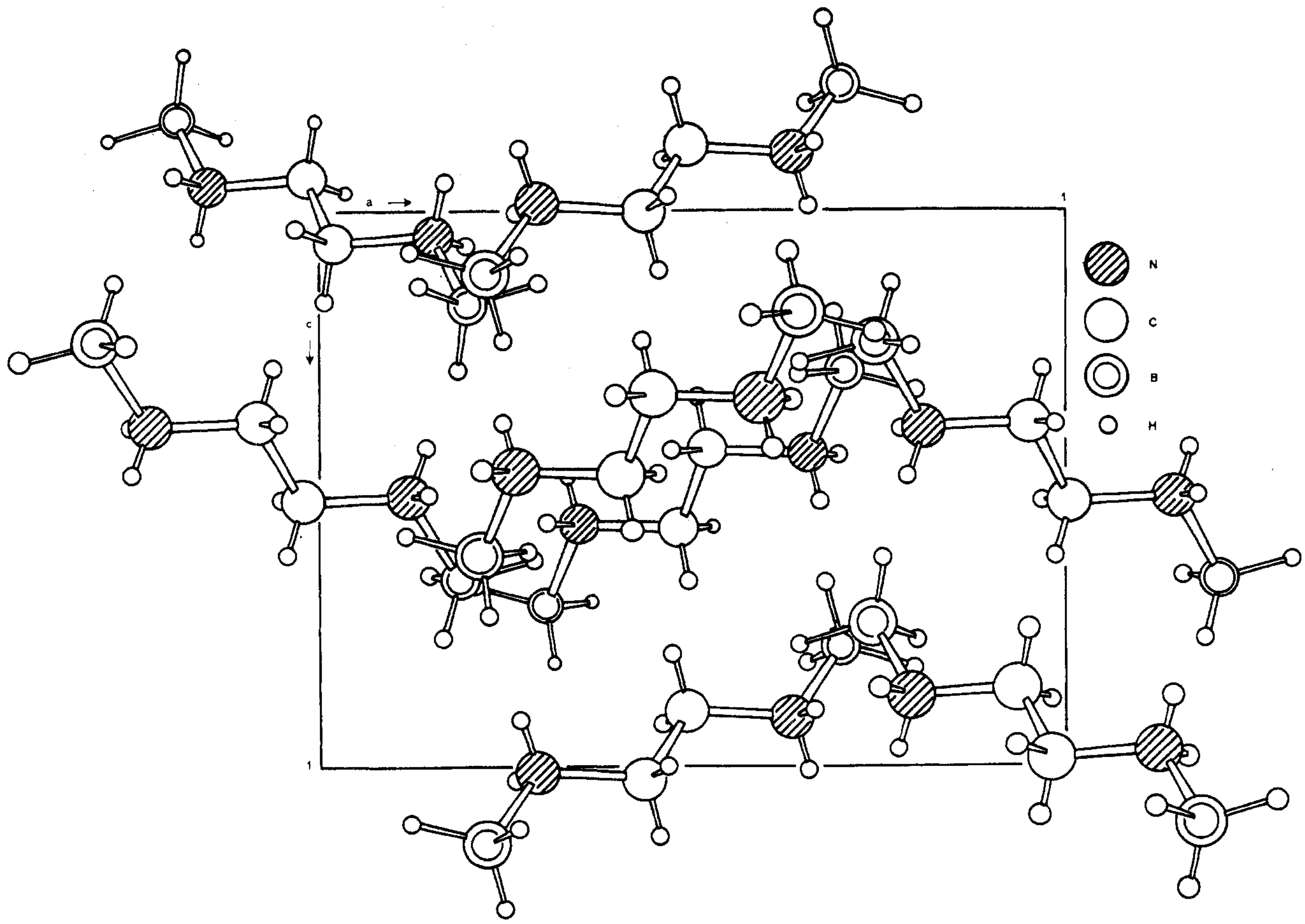

Figure 2.—Unit cell contents of ethylenediamine–bisborane structure projected onto the *ac* plane.

TABLE I

ATOMIC AND THERMAL PARAMETERS FOR ETHANE-1,2-DIAMINE–BORANE[a]

Atom	X	Y	Z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N	0.1594 (3)	0.0835 (5)	0.0548 (5)	2.9 (2)	2.8 (2)	3.2 (2)	−0.4 (3)	0.4 (3)	0.1 (4)
C	0.0238 (4)	0.0584 (6)	0.0651 (6)	2.9 (2)	3.4 (3)	3.6 (3)	−0.4 (4)	−0.1 (4)	−1.1 (4)
B	0.2156 (5)	0.2044 (6)	0.1905 (7)	4.0 (3)	3.1 (3)	4.2 (3)	−1.2 (4)	−1.3 (5)	−0.6 (6)
H(1)	0.179 (3)	0.125 (4)	−0.036 (4)	1.3 (9)					
H(2)	0.195 (3)	−0.010 (5)	0.061 (5)	7.0 (12)					
H(3)	0.007 (3)	0.017 (4)	0.164 (5)	3.0 (10)					
H(4)	−0.015 (3)	0.167 (5)	0.052 (5)	4.1 (10)					
H(5)	0.163 (3)	0.328 (4)	0.172 (4)	3.2 (7)					
H(6)	0.198 (2)	0.144 (4)	0.300 (4)	2.8 (8)					
H(7)	0.312 (3)	0.221 (4)	0.155 (4)	2.7 (8)					

[a] Anisotropic thermal parameters have the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE II

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) FOR ETHANE-1,2-DIAMINE–BORANE

N–C	1.477 (5)	C–H(3)	0.89 (4)
N–B	1.600 (7)	C–H(4)	0.98 (4)
C–C′	1.514 (7)	B–H(5)	1.17 (4)
N–H(1)	0.84 (3)	B–H(6)	1.04 (3)
N–H(2)	0.86 (4)	B–H(7)	1.08 (4)
C–N–B	114.9 (4)	H(3)–C–C′	108.8 (24)
C′–C–N	112.4 (4)	H(4)–C–C′	110.1 (23)
C–N–H(1)	110.8 (21)	H(3)–C–H(4)	111.0 (33)
C–N–H(2)	107.9 (25)	N–B–H(5)	105.2 (16)
B–N–H(1)	105.3 (22)	N–B–H(6)	103.3 (19)
B–N–H(2)	110.1 (27)	N–B–H(7)	104.9 (17)
H(1)–N–H(2)	107.7 (35)	H(5)–B–H(6)	116.1 (25)
H(3)–C–N	107.5 (23)	H(5)–B–H(7)	108.0 (24)
H(4)–C–N	107.0 (22)	H(6)–B–H(7)	117.7 (25)

Discussion

Ethylenediamine–bisborane exists in the trans conformation in the solid state. The molecular structure, along with the bond lengths and angles, is shown in Figure 1. Figure 2 shows the projection of the unit cell contents onto the *ac* plane. The molecules are held together by van der Waals forces.

Symmetry considerations indicate the carbon and nitrogen atoms must define a plane; however, the boron atoms are not restricted to this plane. A least-squares plane fitted to nonhydrogen atoms of the molecule shows the molecule is planar with a deviation of 0.005 Å.

The C–C distance of 1.514 (7) Å is normal and falls well within the range of 1.50–1.55 Å found for several bidentate ethylenediamine complexes.[7] The N–C distance of 1.477 (5) Å is equivalent to the value of 1.50 (2) Å reported for monomethylamine–boron trifluoride,[8] $(CH_3)H_2N\cdot BF_3$, and trimethylamine–boron trifluoride,[9] $(CH_3)_3N\cdot BF_3$. Although the variations are not statistically significant, some differences in bond lengths are expected due to differences in acceptor properties. The N–C distance also falls within the range 1.44–1.50 Å reported for a series of ethylenediamine–metal complexes.[6]

The N–B distance of 1.600 (7) Å may be compared with the values of 1.60 (2) Å ($H_3N\cdot BF_3$), 1.57 (2) Å ($(CH_3)H_2N\cdot BF_3$), and 1.58 (3) Å ($(CH_3)_3N\cdot BF_3$).[10] Methyl substituents increase molecular stability which is reflected in a shortening of the N–B distance; however, steric interaction in the trimethyl compound reverses this trend. Since BH_3 is a weaker acceptor than BF_3, the $N–BH_3$ distance should be longer than the corresponding $N–BF_3$. Although the bond lengths are not statistically different, the N–B distance in ethylenediamine–bisborane is longer than the distance in comparable BF_3 adducts.

The apparent average bond distances involving hydrogen are B–H = 1.10 Å, N–H = 0.85 Å, and C–H = 0.94 Å. The average angles are CNH = 110°, BNH = 108°, NCH = 107°, HCC = 110°, and NBH = 104°. The CNB angle is 114.9 (4)° and the CCN angle is 112.4 (4)°. All of these values are normal.

The ethylenediamine–bisborane molecule approximates C_{2h} symmetry in the solid state. This symmetry leads to 27 infrared-active fundamental vibrations, none of which is Raman active. Small deviations from C_{2h} symmetry may permit other vibrations to appear as weak bands. Since the infrared spectrum was assigned on the basis of a gauche conformation, a reanalysis of the spectrum is required.

Acknowledgment.—We wish to express our appreciation to the TCU Research Foundation for their financial assistance.

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
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The Crystal Structure of Tetraethylammonium 2,2'-*commo*-Bis(nonahydrodicarba-2-cobalta-*closo*-decaborate), a Salt of the Cobalt Derivative of the Nonahydridodicarbanonaborate(2−) Ligand[1]

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The crystal structure of $(C_2H_5)_4NCo(B_7C_2H_9)_2$, the tetraethylammonium salt of 2,2'-*commo*-bis(nonahydrodicarba-2-cobalta-*closo*-decaborate)(1−), has been determined from X-ray diffraction data measured from a single crystal by counter methods. The crystals are tetragonal, space group $P4/n$, with $a = 16.556$ (6), $c = 8.580$ (4) Å, $Z = 4$, $d_x = 1.15$ g/cm³. Refinement by least squares reduced R to 0.097 for 926 reflections. The anion is a sandwich compound of cobalt with two carborane polyhedral fragments, in the shape of two distorted bicapped square antiprisms with one vertex (occupied by the cobalt atom) in common. Disorder exists for the location of half of the carbon atoms in the carborane cages and for the orientation of half of the tetraethylammonium ions. Average bond lengths (excluding atoms involved in disorder) are Co–C = 1.93, Co–B = 2.15, B–C (polar) = 1.60, B–B (polar) = 1.73, B–B (tropical) = 1.88, B–B (equatorial) = 1.83 Å.

Introduction

A new polyhedral transition metal complex containing the $B_7C_2H_9^{2-}$ ligand was prepared by Hawthorne and George,[2] who deduced its structure on the basis of nmr data and chemical analysis. The anion $Co(B_7C_2H_9)_2^-$, 2,2'-*commo*-bis(nonahydrodicarba-2-cobalta-*closo*-decaborate)(1−), is shown without hydrogen atoms in Figure 1. It is a sandwich compound of cobalt (formal oxidation state 3+) with two carborane polyhedral fragments. Carbon is in position 1 and in either position 6 or position 9 (Figure 1). Positions 6 and 9 are chemically equivalent in each cage but enantiomeric, and isomerism is possible depending on the relationship of the carbon atoms in the two cages of a complex.

This paper describes an X-ray diffraction analysis of the structure of tetragonal crystals of the tetraethylammonium salt of $Co(B_7C_2H_9)_2^-$. This study confirms the structural features found by Hawthorne and George[2] but fails to resolve the isomer problem because disorder is present. A monoclinic phase also present in the sample has not yet been fully characterized.

Experimental Section

Dark red crystals, provided by Professor Hawthorne, were a mixture of plates and needles. The plates, the subject of the present investigation, were flat prisms with {001} as the larger faces and {110} as the only other prominent form. Preliminary information was obtained from oscillation and Weissenberg photographs of a crystal mounted with [110] as the rotation axis, using Cu radiation. The systematic absences ($hk0$ absent if $h + k = 2n + 1$) were confirmed with a manually operated General Electric XRD-5 diffractometer with a quarter-circle Eulerian-cradle goniostat and a scintillation counter with pulse height discriminator. Mo radiation was used with a 0.003 in. thick Zr filter in front of the receiving slit. Cell dimensions were de-

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[1] Work done under the auspices of the U. S. Atomic Energy Commission

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