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Crystal and Molecular Structure of a Tetracarbon Carborane, $(CH_3)_4C_4B_8H_8$, a New Type of Nido Cage System

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The structure of 2,3,7,8-tetramethyl-2,3,7,8-tetracarbadodecaborane(12) $[(CH_3)_4C_4B_8H_8]$, a carborane formed by air oxidation of $[(CH_3)_2C_2B_4H_4]_2CoH$ or $[(CH_3)_2C_2B_4H_4]_2FeH_2$, has been determined from a single-crystal x-ray diffraction study. The molecule is a distorted icosahedron, in which two carbon–carbon bonds have been severed to create two four-sided open faces, and consists of two pyramidal $(CH_3)_2C_2B_4H_4$ units fused face-to-face with the four skeletal carbon atoms forming a contiguous chain. The polyhedral cage contains two more electrons than the icosahedral $C_2B_{10}H_{12}$ system and is isoelectronic with the $C_2B_{10}H_{12}^{2-}$ ion. The geometry of $(CH_3)_4C_4B_8H_8$ differs sharply from those of the only other structurally established 12-vertex nido systems, $(C_6H_5)_2C_2B_{10}H_{11}^-$ and $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$, each of which has a single large open face. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.398$ (3) Å, $b = 11.420$ (5) Å, $c = 13.458$ (7) Å, $\beta = 90.61$ (4)°, $d_{obsd} = 1.05$ g cm^{-3}, and $d_{calcd} = 1.04$ g cm^{-3} for $Z = 4$. The structure was refined by full-matrix least-squares procedures to a final R value of 0.153. The molecule is discussed in relation to the theory of bonding in polyhedral cages and also in terms of the mechanism of its formation from the metallocarborane precursors.

In earlier papers from this laboratory[1,2] we described the preparation and spectroscopic characterization of a new carborane $(CH_3)_4C_4B_8H_8$ and its use as a ligand in tetracarbon metallocarboranes. Although nearly 3 years has elapsed since its discovery, definitive structural characterization of this molecule eluded us despite the fact that it is an air-stable solid which can be obtained in high yield and purity from the readily prepared complexes[2,3] $[(CH_3)_2C_2B_4H_4]_2FeH_2$ and $[(CH_3)_2C_2B_4H_4]_2CoH$. The proton and boron-11 NMR spectra of $(CH_3)_4C_4B_8H_8$ are complicated by its strange behavior in solution,[1,2] in which an equilibrium is established between two structurally distinct isomers, A and B, one of which (B) is fluxional above 25 °C; on removal of solvent, the compound reverts to a single isomer, A.

The colorless, slightly volatile crystals of A which were grown from various solvents were consistently unsuitable for x-ray structural analysis. Nevertheless, an x-ray study of this compound remained an objective of high priority for several reasons: (1) The molecule contains two more skeletal electrons than the icosahedral $C_2B_{10}H_{12}$ system, and a structural comparison with the latter molecule was a matter of considerable interest. (2) No carborane having more than two carbon atoms in the same polyhedron had been crystallographically characterized (the small species $C_4B_2H_6$ and $(CH_3)_6C_4B_2$ have been examined respectively by microwave[4] and electron diffraction[5] spectroscopy). (3) The formation of $(CH_3)_4C_4B_8H_8$ by oxidative fusion of $(CH_3)_2C_2B_4H_4^{2-}$ ligands from the above-mentioned cobalt and iron complexes[2,3] is a novel and potentially significant synthetic process whose steric details warrant examination. (4) Recent synthetic work has shown that $(CH_3)_4C_4B_8H_8$ is the prototype of a large family of tetracarbon carborane[6] and metallocarborane[7,8] cage systems.

After many attempts entailing considerable difficulty we succeeded in obtaining a few usable crystals, which were still of relatively poor quality but which did permit x-ray determination of the cage geometry and connectivity. Data collection, solution, and refinement were conducted on two crystals grown from separate samples of the compound, yielding the results which we now report.

Experimental Section

Repeated attempts to grow single crystals from a variety of common solvents produced only soft needles which were very poor diffractors of x rays and could not be used for data collection. Eventually, very slow evaporation from hexane solution over a period of weeks produced relatively hard rhomboids which gave diffraction photographs of satisfactory quality. The first crystal selected was mounted on a glass fiber open to the air. The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then employed in the program INDEX to obtain appropriate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged acceptable. Crystal data for $C_8B_8H_{20}$ are as follows: mol wt 202.7; space group $P2_1/n$; $a = 8.398$ (3), $b = 11.420$ (5), $c = 13.458$ (7) Å; $\beta = 90.61$ (4)°; $V = 1291$ Å^3; $Z = 4$; $d_{calcd} = 1.04$, $d_{obsd} = 1.05$ g cm^{-3}; μ(Mo Kα) = 0.5 cm^{-1}.

The space group chosen, $P2_1/n$, is an alternative setting of the conventional space group $P2_1/c$ (No. 14) and has the general equivalent positions x, y, z; $-x, -y, -z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$.

Collection and Refinement of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP-8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1 < 2\theta < 44°$. The scan widths (SW) used are given by SW = $A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to Kα_1–Kα_2 splitting. The values of A and B were 0.70 and 0.30°, respectively. The calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count was then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the calculated peak intensity. Intensities which registered less than 8 counts above background on a rapid prescan were considered insignificant and were rejected automatically by the computer.

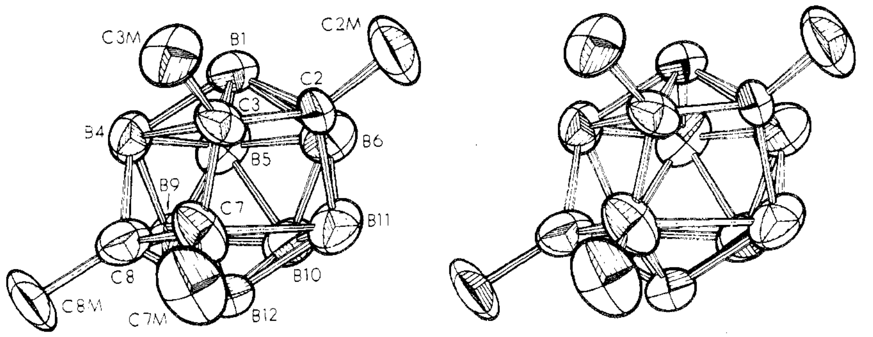

Figure 1. Stereodrawing of the molecular structure of $(CH_3)_4C_4B_8H_8$, showing nonhydrogen atoms as 50% probability ellipsoids.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom[b]	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C2	0.109 (1)	0.835 (1)	0.1316 (9)	0.007 (2)	0.007 (1)	0.0069 (9)	0.006 (3)	−0.000 (2)	0.003 (2)
C2M	−0.020 (2)	0.903 (1)	0.1818 (13)	0.013 (3)	0.013 (2)	0.0115 (13)	0.008 (4)	−0.001 (3)	−0.002 (3)
C3	0.236 (1)	0.772 (1)	0.1803 (9)	0.010 (2)	0.005 (1)	0.0064 (8)	0.003 (3)	0.005 (2)	−0.004 (2)
C3M	0.236 (2)	0.747 (1)	0.2926 (8)	0.028 (3)	0.013 (2)	0.0010 (6)	0.003 (4)	0.001 (3)	0.000 (2)
C7	0.395 (1)	0.812 (1)	0.1378 (10)	0.009 (2)	0.008 (1)	0.0079 (9)	0.001 (3)	−0.000 (2)	−0.009 (2)
C7M	0.498 (2)	0.890 (1)	0.1986 (12)	0.015 (3)	0.009 (1)	0.0117 (13)	−0.003 (4)	−0.006 (3)	−0.006 (3)
C8	0.461 (2)	0.703 (1)	0.0912 (10)	0.018 (3)	0.005 (1)	0.0065 (9)	−0.005 (3)	0.007 (3)	0.001 (2)
C8M	0.637 (2)	0.661 (1)	0.1065 (4)	0.007 (2)	0.010 (1)	0.0178 (17)	0.006 (3)	0.003 (3)	−0.000 (3)
B1	0.101 (2)	0.691 (1)	0.116 (1)	0.010 (3)	0.009 (2)	0.0064 (11)	−0.004 (4)	−0.002 (3)	0.004 (2)
B4	0.296 (2)	0.618 (1)	0.097 (1)	0.015 (3)	0.006 (1)	0.0066 (11)	0.003 (4)	0.000 (3)	0.002 (2)
B5	0.170 (2)	0.658 (1)	−0.010 (1)	0.021 (3)	0.006 (1)	0.0046 (10)	−0.007 (4)	−0.005 (3)	−0.001 (2)
B6	0.071 (2)	0.793 (2)	0.012 (1)	0.023 (4)	0.011 (2)	0.0047 (10)	0.003 (5)	0.003 (3)	0.005 (3)
B9	0.368 (2)	0.676 (2)	−0.019 (1)	0.017 (3)	0.010 (2)	0.0050 (9)	0.003 (4)	0.004 (3)	0.002 (2)
B10	0.241 (2)	0.796 (1)	−0.056 (1)	0.021 (3)	0.006 (1)	0.0078 (11)	0.000 (4)	0.011 (3)	0.001 (2)
B11	0.225 (2)	0.892 (1)	0.038 (1)	0.024 (4)	0.008 (1)	0.0043 (9)	0.006 (4)	0.009 (3)	0.003 (2)
B12	0.412 (2)	0.820 (1)	0.019 (1)	0.013 (3)	0.008 (2)	0.0067 (11)	−0.003 (4)	0.003 (3)	0.004 (2)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H1	−0.04 (2)	0.66 (1)	0.122 (9)	10 (4)	H22	0.01 (2)	0.96 (1)	0.203 (9)	6
H4	0.34 (2)	0.53 (1)	0.113 (9)	6	H23	−0.08 (2)	0.90 (1)	0.121 (9)	6
H5	0.12 (1)	0.59 (1)	−0.048 (8)	5 (3)	H31	0.25 (2)	0.78 (1)	0.335 (9)	6
H6	0.01 (2)	0.82 (1)	−0.032 (10)	10 (4)	H33	0.39 (2)	0.69 (1)	0.356 (9)	6
H9	0.46 (1)	0.62 (1)	−0.092 (9)	5	H32	0.14 (2)	0.71 (1)	0.329 (9)	6
H11	0.23 (2)	1.00 (2)	0.005 (11)	8 (4)	H71	0.47 (2)	0.90 (1)	0.273 (9)	6
H12	0.51 (1)	0.86 (1)	−0.008 (9)	4 (3)	H72	0.54 (2)	0.94 (1)	0.190 (9)	6
H21	−0.06 (1)	0.85 (1)	0.260 (8)	8 (3)	H73	0.59 (2)	0.84 (1)	0.246 (9)	6

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. [b] The methyl hydrogen atoms are labeled H21, H22, H23, H31, H32, H33, H71, H72, and H73, corresponding to their attachment to C2M, C3M, and C7M, respectively. Atoms H10, H81, H82, and H83 were not found.

The intensities of three standard reflections, monitored at 100 reflection intervals, showed considerable (~70%) deterioration of the crystal during data collection. The MULTAN 74[9] program series was used to attempt a solution of the phase problem. All observed F's were used as input to NORMAL, and the 250 highest E values (together with the 28 lowest, for ψ_0 testing) were used in MULTAN. Although the distribution of E values was poor and suggested an acentric rather than a centric structure (an impossibility), the phase set with the highest figure of merit was correct, and an E map gave the positions of all 16 nonhydrogen atoms in the asymmetric unit, allowing an unequivocal assignment of atom types to the peaks. The atom positions were inserted, and an R value of 0.24 was obtained before refinement. At this point a new crystal was mounted in a glass capillary under dry nitrogen and the above data collection procedure was repeated. The new data set was better than that collected from the first crystal, although still less than ideal, and the first data were not further used. The data were corrected for crystal deterioration (~50%) from the standard intensity scans using the program CHORTA (K. O. Hodgson, Stanford University), which allows for anisotropic intensity variation. The raw intensity data were corrected for Lorentz and polarization factors (Lp) (including the polarization effect of the crystal monochromator). After averaging of the intensities of equivalent reflections, the data were reduced to 1541 independent intensities of which 942 had $F_o^2 > 3\sigma(F_o^2)$ where $\sigma(F_o^2)$ was estimated from counting statistics.[10] These data were used in the final refinement of the structural parameters.

Refinement of the Structure. The positions of the nonhydrogen atoms phased the intensity data well enough to permit the location of most of the hydrogen atoms from a Fourier difference function. These positions were included in the refinement, and anisotropic temperature factors were introduced for all nonhydrogen atoms. Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[11] and those for hydrogen from Stewart et al.[12] The effects of anomalous dispersion for nonhydrogen atoms were included in F_c using Cromer and Ibers' values[13] for $\Delta f'$ and $\Delta f''$. Agreement factors were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The model converged with $R = 0.153$ and $R_w = 0.164$. The largest parameter shift was less than 0.1 of its estimated standard deviation, and the error in an observation of unit weight was 2.9. A final Fourier difference map was featureless. A table of the observed and calculated structure factors is available, (supplementary material). Despite the high R value resulting from marginal crystal quality, the atom connectivities and approximate bond lengths are unequivocally established. The main chemical objective of the structure determination having been achieved, it did not appear likely that data collection on still other crystals would significantly improve the level of precision and consequently none was attempted.

Results and Discussion

The molecular structure and packing diagram are shown in Figures 1 and 2, respectively, with final positional and thermal parameters, bond lengths, and angles given in Tables

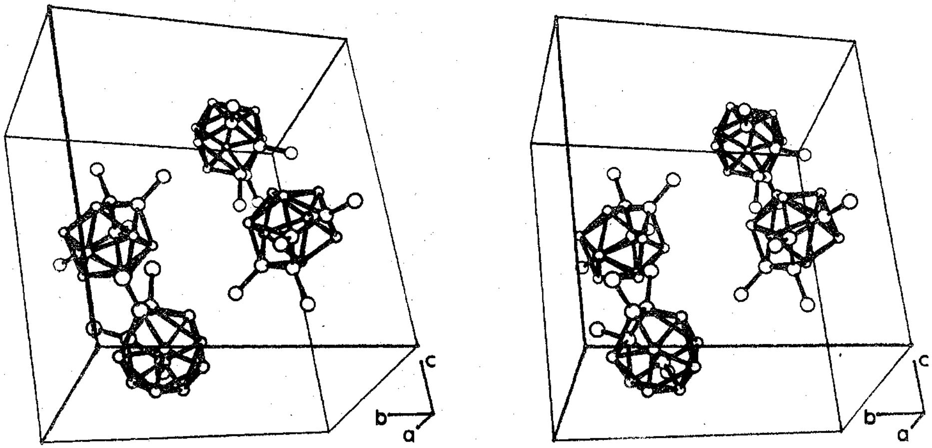

Figure 2. Stereodrawing of the unit cell contents.

Table II

	Bond Distances, Å		
C2–C2M	1.50 (2)	C8–B12	1.71 (1)
C2–C3	1.43 (1)	B1–B4	1.86 (2)
C2–B1	1.66 (1)	B1–B5	1.84 (2)
C2–B6	1.70 (1)	B1–B6	1.83 (2)
C2–B11	1.73 (1)	B4–B5	1.83 (2)
C3–C3M	1.54 (1)	B4–B9	1.82 (1)
C3–C7	1.53 (1)	B5–B6	1.78 (2)
C3–B1	1.70 (1)	B5–B9	1.69 (1)
C3–B4	2.15 (1)	B5–B10	1.80 (1)
C7–C7M	1.48 (1)	B6–B10	1.70 (2)
C7–C8	1.50 (1)	B6–B11	1.75 (2)
C7–B11	2.15 (1)	B9–B10	1.80 (2)
C7–B12	1.62 (1)	B9–B12	1.76 (2)
C8–C8M	1.57 (1)	B10–B11	1.68 (1)
C8–B4	1.69 (1)	B10–B12	1.76 (2)
C8–B9	1.70 (1)	B11–B12	1.79 (2)
	Nonbonded Distances, Å		
C2–C7	2.42 (1)	C3–C8	2.39 (1)
C3–B11	2.35 (1)	B4–C7	2.42 (1)

I–III. The cage is a polyhedron with two four-sided open faces bounded respectively by C2, C3, C7, and B11 and by C3, C7, C8, and B4 and can be described as an icosahedron which has been distorted by stretching the C2–C7 and C3–C8 connections to give the nonbonding distances 2.42 (1) and 2.39 (1) Å, respectively; in addition, C7–B11 (2.15 (1) Å) and C3–B4 (2.15 (1) Å) are unusually long boron–carbon links. The molecule lacks rigorous crystallographic symmetry, but the pseudo-C_2 axis passing through the midpoints of the C3–C7 and B5–B10 bonds is in accord with previous NMR observations[1,2] which indicated either C_2 or C_s symmetry in solution. There are no intermolecular distances (nonhydrogen atoms) within 3.6 Å.

The observed solid-state structure is very close to the geometry which we had formerly suggested[1,2] for isomer B on the basis of solution NMR data and differs substantially from the more open structure which has been postulated for isomer A. Since the isomer existing in the solid state must be presumed to be A (from the fact that only the ^{11}B and ^1H spectra of A are seen when the solid compound is first placed in solution[14]), the actual structure of B remains an open question; the matter is further complicated by the observed fluxional behavior of B which renders all four C–CH_3 groups equivalent on the NMR time scale at +40 °C and above.[2] Isolation of a crystalline sample of B at low temperature remains a possible avenue for resolution of this question.

Returning to the structure of A, the molecule can be viewed as two pentagonal-pyramidal $(CH_3)_2C_2B_4H_4$ units fused face-to-face, obviously reflecting its synthesis[2,3] from $[(CH_3)_2C_2B_4H_4]_2CoH$ and from $[(CH_3)_2C_2B_4H_4]_2FeH_2$. It is significant that the fusion occurs such as to place the four cage carbons in close proximity, since this suggests that linkage of the C_2B_4 units to each other commences *before* they are separated from the metal atom, i.e., while the relative alignment of the ligands is still controlled by their bonds to the metal. If two *independent* C_2B_4 moieties were to fuse, one would expect the two pairs of carbon atoms to adopt trans, or at least nonvicinal, locations in the product; this would be anticipated on grounds of electrostatic C–C repulsion and would be expected to relieve possible steric crowding of the methyl groups. That this is not observed undoubtedly means that the ligands in the precursor metal complexes are aligned in cis fashion with their respective CH_3CCCH_3 groups on the same side of the molecule. We had suspected earlier that this was the case since an x-ray study[15] of the closely related species $(\eta^5\text{-}C_5H_5)CoFe[(CH_3)_4C_4B_8H_8]$, which was prepared by insertion of a $(C_5H_5)Co$ unit into $[(CH_3)_4C_2B_4H_4]_2FeH_2$, has shown that the CH_3C–CCH_3 groups are in a cis orientation.

From our point of view, the aspect of the present structure which is of primary interest is the nature of the distortion from icosahedral symmetry as described above. Well-established correlations[16] between geometry and the number of framework electrons, *e*, indicate that an *n*-vertex polyhedron in which $e = 2n + 2$ will adopt a closo shape (all faces triangular) but that when $e > 2n + 2$, a structure having one or more open (i.e., nontriangular) faces will result. The theoretical basis for this rule,[16] stated simply, is that closo polyhedra have $n + 1$ bonding orbitals in the skeletal framework, and any electrons in excess of $2n + 2$ will occupy antibonding orbitals and thereby produce cage-opening or other distortion.

The $(CH_3)_4C_4B_8H_8$ structure is a $2n + 4$ system with 28 skeletal electrons, isoelectronic with the known $C_2B_{10}H_{12}^{2-}$ and $C_2B_{10}H_{13}^-$ ions[17] and the hypothetical $B_{12}H_{12}^{4-}$ species. The structure of the $C_2B_{10}H_{12}^{2-}$ ion (in any of its isomeric forms) is not known, but as a ligand in 13-vertex transition metal metallocarboranes such as $(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$[18] and the $[(CH_3)_2C_2B_{10}H_{10}]_2Ti^{2-}$ ion,[19] the $C_2B_{10}H_{12}^{2-}$ moiety has a six-membered open face coordinated to the metal. Protonation of $C_2B_{10}H_{12}^{2-}$ yields the $C_2B_{10}H_{13}^-$ ion,[17b,e] whose *C,C′*-diphenyl derivative has been shown from x-ray data[20] to consist of an 11-vertex CB_{10} cage with a five-membered open face; bridging a B–B bond on this face is a methylenic C_6H_5CH group. Thus, one carbon atom in the C_2B_{10} framework has moved out of the cage proper into a bridge location. The only other structurally established 12-atom $2n + 4$ system is a tetracarbon ferracarborane,[8] $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_7H_8$, which contains a 12-vertex FeC_4B_7 cage having a large, six-membered open face.

In contrast to these other 28-electron, 12-atom frameworks, $(CH_3)_4C_4B_8H_8$ reflects a rather more subtle distortion from

Table III. Bond Angles (deg)

C2M–C2–C3	126.0 (9)	B4–B9–B12	99.2 (7)
C2M–C2–B1	123.0 (8)	C3–C7–B12	118.5 (8)
C2M–C2–B6	116.5 (9)	C8–C7–B11	109.6 (7)
C2M–C2–B11	123.2 (9)	C8–C7–B12	66.2 (6)
C3–C2–B1	66.1 (6)	B11–C7–B12	54.5 (7)
C3–C2–B6	114.8 (7)	C8M–C8–C7	123.3 (8)
C3–C2–B11	95.5 (6)	C8M–C8–B4	126.5 (7)
B1–C2–B6	66.1 (6)	C8M–C8–B9	118.8 (8)
B1–C2–B11	107.8 (7)	C8M–C8–B12	122.2 (8)
B6–C2–B11	61.3 (6)	C7–C8–B4	98.4 (7)
C3M–C3–C2	122.4 (8)	C7–C8–B9	110.3 (8)
C3M–C3–C7	115.5 (8)	C7–C8–B12	60.1 (6)
C3M–C3–B1	112.9 (7)	B4–C8–B9	64.8 (6)
C3M–C3–B4	110.9 (7)	B4–C8–B12	106.6 (7)
C2–C3–C7	109.4 (8)	B9–C8–B12	62.2 (6)
C2–C3–B1	63.3 (6)	C2–B1–C3	50.6 (6)
C2–C3–B4	110.3 (7)	C2–B1–B4	115.1 (8)
C7–C3–B1	123.7 (7)	C2–B1–B5	107.9 (8)
C7–C3–B4	80.5 (7)	C2–B1–B6	58.1 (6)
B1–C3–B4	56.3 (7)	C3–B1–B4	74.2 (6)
C7M–C7–C3	118.7 (7)	C3–B1–B5	111.5 (7)
C7M–C7–C8	120.6 (8)	C3–B1–B6	97.0 (7)
C7M–C7–B11	118.2 (7)	B4–B1–B5	59.6 (6)
C7M–C7–B12	117.1 (9)	B4–B1–B6	106.9 (7)
C3–C7–C8	103.8 (7)	B5–B1–B6	57.9 (6)
C3–C7–B11	77.6 (7)	C3–B4–C8	75.9 (6)
C3–B4–B5	94.1 (7)	C3–B4–B9	103.6 (7)
C3–B4–B1	49.6 (6)	B5–B9–B10	62.1 (6)
B5–B4–B1	59.6 (6)	B5–B9–B12	107.4 (7)
B5–B4–C8	106.8 (7)	B10–B9–B12	59.4 (6)
B5–B4–B9	55.1 (6)	B5–B10–B6	60.9 (7)
B1–B4–C8	118.6 (6)	B5–B10–B9	55.9 (7)
B1–B4–B9	105.1 (7)	B5–B10–B11	106.6 (7)
C8–B4–B9	57.8 (7)	B5–B10–B12	102.3 (6)
B1–B5–B4	60.8 (7)	B6–B10–B9	109.6 (7)
B1–B5–B10	104.3 (7)	B6–B10–B11	62.5 (7)
B1–B5–B6	61.0 (6)	B6–B10–B12	112.3 (6)
B1–B5–B9	111.6 (7)	B9–B10–B11	110.0 (7)
B4–B5–B6	110.3 (7)	B9–B10–B12	59.1 (7)
B4–B5–B9	61.9 (6)	B11–B10–B12	62.7 (7)
B4–B5–B10	107.1 (7)	C2–B11–B6	58.5 (6)
B6–B5–B9	111.5 (8)	C2–B11–C7	76.1 (7)
B6–B5–B10	56.8 (6)	C2–B11–B10	110.4 (6)
B9–B5–B10	62.1 (7)	C2–B11–B12	115.8 (7)
C2–B6–B1	55.8 (7)	C7–B11–B6	109.3 (7)
C2–B6–B5	108.7 (8)	C7–B11–B10	97.8 (7)
C2–B6–B10	110.8 (7)	C7–B11–B12	47.4 (7)
C2–B6–B11	60.3 (7)	B6–B11–B10	59.5 (6)
B1–B6–B5	61.1 (6)	B6–B11–B12	108.7 (7)
B1–B6–B10	108.5 (7)	B10–B11–B12	61.0 (7)
B1–B6–B11	99.7 (7)	C7–B12–C8	53.7 (7)
B5–B6–B10	62.3 (8)	C7–B12–B9	102.3 (8)
B5–B6–B11	104.5 (7)	C7–B12–B10	118.2 (7)
B10–B6–B11	58.1 (6)	C7–B12–B11	78.1 (6)
C8–B9–B4	57.4 (6)	C8–B12–B9	58.7 (7)
C8–B9–B5	113.4 (7)	C8–B12–B10	113.0 (7)
C8–B9–B10	111.6 (7)	C8–B12–B11	118.8 (6)
C8–B9–B12	59.1 (7)	B9–B12–B10	61.5 (7)
B4–B9–B5	63.0 (7)	B9–B12–B11	106.9 (7)
B4–B9–B10	107.9	B10–B12–B11	56.3 (7)

regular icosahedral geometry. It has been noted elsewhere[21] that although the addition of electrons to a $2n + 2$ closo system usually opens the polyhedron to produce a single large hole, the distortion need not always occur in this way. Thus, the trigonal-bipyramidal species $(\eta^5\text{-}C_5H_5)_3Ni_3S_2$[22] and $(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$[23] (which are $2n + 7$ and $2n + 3$ systems, respectively) were cited[21a] as examples in which the excess electrons enter antibonding orbitals[22] to produce equal lengthening of all three Ni–Ni bonds, rather than selective rupture of one particular link which would have produced square-planar geometry; consequently the D_{3h} symmetry in these species is preserved, but with lengthening of the equatorial bonds. Similar "stretch–distortion" effects have since been noted in several metallocarboranes.[24] As far as we are aware, however, $(CH_3)_4C_4B_8H_8$ is the first clear example of this alternative type of nido structure in an exclusively nonmetal borane or carborane, in that all other such species either are completely closed or else have a single well-defined five- or six-membered open face.

It is possible to account for the observed geometry in terms of a few simple qualitative ideas. The icosahedron is obviously a highly favored shape for those 12-atom clusters that can meet the electronic requirement[16] of 26 framework valence electrons and indeed is a pervasive theme in boron chemistry from the metal borides to the carboranes and metallocarboranes. The tendency to achieve icosahedral symmetry is strongly felt in $(CH_3)_4C_4B_8H_8$, which has no bridging hydrogen atoms or other features which might sterically interfere with polyhedral closure, but the two "extra" skeletal electrons prevent its full achievement; the result is a compromise in which the electronically induced distortion from icosahedral symmetry is minimized, taking the form of stretching two C–C interactions to the point of severing. Selective cleavage of C–C rather than C–B or B–B links can be rationalized in terms of mutual electrostatic repulsion of the relatively positive carbon nuclei, which is to say if something has to break, it is most likely to be a carbon–carbon bond. An additional factor is surely the absence of "extra" hydrogen atoms in the molecule. As we noted earlier, the $(C_6H_5)_2C_2B_{10}H_{11}^-$ ion and $(\eta^5\text{-}C_5H_5)Fe(CH_3)_4C_4B_8H_8$ are the only other examples of 12-vertex nido cages, and each contains an extra hydrogen which is located in the vicinity of the open face and checks any tendency toward partial cage closure. Lipscomb[20,25] has suggested that the $C_2B_{10}H_{12}^{2-}$ ion, which lacks bridging hydrogens, retains a closo configuration and differs sharply from its protonated derivative. The present results on a tetracarbon analogue of this ion clearly support this hypothesis.

Future synthetic and structural studies of related molecules can be expected to sharpen, modify, and perhaps reject some of the ideas expressed here.

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Supplementary Material Available: Listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Inorganic Derivatives of Iron–Sulfide–Thiolate Dimers and Tetramers. Structures of Tetrachloro-μ-disulfido-diferrate(III) and Tetrakis(chloro-μ_3-sulfido-iron) Dianions

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Reaction of benzoyl chloride with the complexes $[Fe_2S_2(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ affords $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_4S_4Cl_4]^{2-}$, respectively, which are members of a complete set of new dimeric and tetrameric inorganic dianions with terminal chloride, bromide, and iodide ligands. The structures of the tetraethylammonium salts of the chloride dimer and tetramer have been determined. Both compounds crystallize in space group $P2_1/c$ (C_{2h}^5) of the monoclinic system with dimensions a = 8.842 (2) Å, b = 10.186 (2) Å, c = 15.985 (3) Å, and β = 109.28 (2)° for the dimer salt (Z = 2) and a = 13.600 (7) Å, b = 12.895 (9) Å, c = 18.707 (5) Å, and β = 110.29 (3)° for the tetramer salt (Z = 4). Anion structures are nearly identical with those previously determined for their thiolate precursors. $[Fe_2S_2Cl_4]^{2-}$ has crystallographically imposed centrosymmetry and is formed by S···S edge sharing of two tetrahedra. The Fe···Fe and mean Fe–S and Fe–Cl distances are 2.716, 2.201, and 2.252 Å, respectively; bond angles at Fe vary from 103.8 to 112.7°. $[Fe_4S_4Cl_4]^{2-}$ exhibits cubane-type stereochemistry but is distorted from T_d to effective D_{2d} symmetry. The bonded Fe–S distances occur as sets of four (2.260 (3) Å) and eight (2.295 (3) Å), giving an average of 2.283 Å; the average Fe–Cl distance is 2.216 (2) Å. The Fe_4 unit is nearly tetrahedral with an average Fe···Fe distance of 2.766 (5) Å. These structures are compared with those of thiolate dimer and tetramer dianions, revealing that Fe_2S_2 and Fe_4S_4 core structures are nearly invariant to the nature of the terminal ligands. Dimer–tetramer structural comparisons in both the chloride and thiolate series show larger core distances and smaller terminal ligand distances in the tetramers; these differences are believed to arise mainly from electronic properties rather than from steric effects of terminal ligands.

Introduction

Our past and continuing investigations of iron–sulfur complexes of the general types $[Fe(SR)_4]^{-,2-}$, $[Fe_2S_2(SR)_4]^{2-}$, and $[Fe_4S_4(SR)_4]^{2-,3-}$ have emphasized their utility as synthetic analogues of the active sites of iron–sulfur proteins in equivalent oxidation levels.[1-5] Much of this work has recently been reviewed.[1,2] In examinations of the reactivity properties of binuclear and tetranuclear dianions, certain results have proven and other observations have implied the existence of a substantial body of reaction chemistry involving substitution of terminal thiolate ligands with retention of planar Fe_2S_2 and cubane-type Fe_4S_4 core structures. The species $[Fe_2S_2(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ react cleanly with excess thiol R′SH affording the correspondingly substituted complexes $[Fe_2S_2(SR')_4]^{2-}$[6] and $[Fe_4S_4(SR')_4]^{2-}$,[7] respectively. Such reactions form the basis of the core extrusion method for identification of active sites in iron–sulfur proteins.[8] A study of the tetrameric anion $[Fe_4S_4(SCH_2CH_2CO_2)_4]^{6-}$ in aqueous solution has shown the existence of solvolytic reactions and led to the preliminary kinetic order $Cl^- \sim Br^- < OH^- < CN^-$ for displacement of coordinated thiolate by other nucleophiles.[9] Product species were not isolated. A final observation of pertinence is that reaction of $[Fe_4S_4(SEt)_4]^{2-}$ with benzoyl chloride affords the thioester PhCOSEt;[10] the fate of the Fe_4S_4 portion of the reactant was not ascertained. This reaction displays the nucleophilic reactivity of coordinated thiolate, a property obligatory to the proposed mechanism of thiolate substitution by R′SH.[11] Analogy with this reaction suggested that the other reaction product from benzoyl chloride should be $[Fe_4S_4Cl_4]^{2-}$. This point has been confirmed by product isolation.[12] In addition it has been shown that the dimeric complexes $[Fe_2S_2(SR)_4]^{2-}$ undergo equally facile reactions with benzoyl halides. These reactions, together with halide substitution reactions, have led to isolation of a series of new, fundamental, and strictly inorganic anions of the types $[Fe_4S_4X_4]^{2-}$ and $[Fe_2S_2X_4]^{2-}$ (X^- = Cl^-, Br^-, I^-). The synthesis and properties of these complexes will be described elsewhere.[12] Here we detail the structures of the tetraethylammonium salts of $[Fe_2S_2Cl_4]^{2-}$ and $[Fe_4S_4Cl_4]^{2-}$ and compare these with the structures of their binuclear and tetranuclear thiolate precursors.

Experimental Section

Crystal Data for $(Et_4N)_2[Fe_2S_2Cl_4]$ and $(Et_4N)_2[Fe_4S_4Cl_4]$. Crystals of both compounds were obtained under anaerobic conditions. $(Et_4N)_2[Fe_2S_2Cl_4]$ was dissolved in a minimal volume of acetonitrile at room temperature and the solution was very slowly cooled to −15