The structure of this mercaptide complex is quite different from that of the disulfide complexes of Ni(II), in which each half ligand is one methylene group shorter. A simple redox mechanism utilizing Ni(II) is not apparent for either ligand system.

The complex of Ni(II) with 2-[(2-pyridylmethyl)amino]ethyl mercaptide, the parent ligand of the disulfide complexes,[2,3] has been prepared. Its stoichiometry, $NiLClO_4 \cdot H_2O$, coupled with preliminary diffraction results which indicate an unusually large asymmetric unit, suggest that it is a large cluster compound, perhaps containing a central Ni_4S_4 "cube", quite a different structure again from that herein reported. Difficulty in obtaining a suitable single crystal has prevented further progress.

The apparent absence of simple structure relationships in these systems suggests that redox processes occur through intermediate states quite dissimilar to these complexes, which form afterwards according to their structural stabilities.

The absolute configuration of the structure was not successfully determined. Beginning with the model refined to convergence with $\Delta f''$ values set equal to zero, the R_2 values calculated without further refinement were 0.031 62 for the structure shown in the figures, and 0.031 65, an insignificantly different value, for the enantiomorphic structure. Subsequent refinement to convergence with nonzero $\Delta f''$ values[21] for Ni (0.285), Cl (0.132), and S (0.110) did not appreciably change the difference between the two R_2 values, 0.030 00 and 0.030 07, respectively. Repetition of this procedure with an entirely independent full-matrix least-squares program, FMLS,[22] verified this result. A comparison of the 51 reflections for which $|F_{c,R} - F_{c,S}| > 2$ with the F_o values did not suggest that one chirality (*R* or *S*) is more likely than the other.

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM 18813-05). We are also indebted to the University of Hawaii Computing Center.

Registry No. $Ni_2(pyCH_2CH_2NHCH_2CH_2S)_2(ClO_4)_2$, 62882-90-0; $pyCH_2CH_2NHCH_2CH_2SH$, 49850-74-0; 2-(β-aminoethyl)pyridine, 2706-56-1; ethylene monothiocarbonate, 20628-59-5.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. L. Gavino, unpublished work, University of Hawaii, Honolulu, 1971. Copies are available from K. Seff.

(2) P. E. Riley and K. Seff, *Inorg. Chem.*, **11**, 2993 (1972).

(3) L. G. Warner, M. M. Kadooka, and K. Seff, *Inorg. Chem.*, **14**, 1773 (1975).

(4) J. N. Brown and L. M. Trefonas, *Org. Prep. Proced.*, **2**, 317 (1970).

(5) T. Ottersen, LP-73 computer program, University of Hawaii, 1973.

(6) E. Hilti, PREABS computer program, University of Hawaii, 1975.

(7) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(8) T. Ottersen, ABSCO computer program, Department of Pharmacy, University of Oslo, 1974.

(9) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 71.

(10) Reference 9, p 148.

(11) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "ALFF, Ames Laboratory Fast Fourier", Iowa State University, 1971.

(12) K. Seff, HFIND computer program, University of Hawaii, 1971.

(13) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(14) J. A. Ibers, NUCLS, full-matrix least squares, Northwestern University, Evanston, Ill., based on ORFLS by W. R. Busing and H. A. Levy.

(15) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(16) C. H. Wei and J. R. Einstein, *Acta Crystallogr., Sect. B*, **28**, 2591 (1972).

(17) (a) J. P. Fackler, Jr., *Prog. Inorg. Chem.*, **21**, 55 (1976); (b) J. P. Fackler, Jr., *Adv. Chem. Ser.*, **No. 150**, 394 (1976).

(18) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

(19) G. A. Barclay, E. M. McPartlin, and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25**, 1262 (1969).

(20) J. P. Fackler and W. J. Zegarski, *J. Am. Chem. Soc.*, **95**, 8566 (1973).

(21) Reference 9, p 149.

(22) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, FMLS, full-matrix least squares, modified by T. Ottersen and K. Seff, 1976.

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Crystal and Molecular Structure of $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$

MARGARET MANGION, W. R. CLAYTON, O. HOLLANDER, and S. G. SHORE*

Received September 28, 1976 AIC60714S

The crystal and molecular structure of $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$ has been determined. Three-dimensional x-ray data were collected on an automated diffractometer with monochromatized Mo Kα radiation. The structure was solved in the space group $P2_1/c$ with four molecules in the unit cell for which a = 10.840 (5) Å, b = 11.629 (6) Å, c = 23.698 (10) Å, and β = 90.15 (3)°. The calculated density is 1.10 g/cm^3. The structure was solved by the heavy atom method and was refined by block-diagonal least squares to a final conventional R index of 0.068 and a weighted R index of 0.075 for 2685 independent reflections for which $I \geq 3\sigma(I)$. The anion $Fe(CO)_4B_7H_{12}^-$ consists of a pentagonal-pyramidal, B_6H_9 structure into which a BH_3 and an $Fe(CO)_4$ group are inserted into nonadjacent basal boron–boron bond sites to form apparent three-center bonds. The $Fe(CO)_4$ and BH_3 groups are located at bridge sites beneath the pentagonal-basal plane of the B_6 framework. The structural data favor a hybridization of iron which more closely approximates dsp^3 than d^{2}sp^3. The closest distance of Fe to a terminal B–H hydrogen is 2.82 (5) Å, thereby suggesting little interaction in terms of Fe–H–B bonding. For the inserted BH_3 group, one of the B–H hydrogens is positioned so as to form a "pseudo" B–H–B bridge with a B_6H_9 framework boron, but the distance of this hydrogen, 1.68 (8) Å, to the framework boron is significantly longer than is observed for normal B–H distances, 1.3 Å, in B–H–B bonds. The $N(n\text{-}C_4H_9)_4^+$ ion has the trans configuration. The δ carbon of the fourth branch is badly disordered. Bond distances and bond angles within the B_6H_9 group and the $N(n\text{-}C_4H_9)^+$ ion appear to be normal.

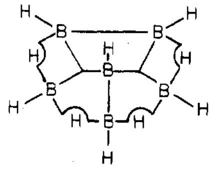
Introduction

The hexaborane(10) molecule is a pentagonal pyramid which can be represented by the valence structure shown below.[1] Hexaborane(10) possesses acidic[2] and basic character.[3] It functions as a Bronsted acid through removal of a bridging proton to yield $B_6H_9^-$, and it functions as a Bronsted

Table I. Fractional Coordinates and Anisotropic Thermal Parameters for Nonhydrogen Atoms of $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$

Atom	10^4x	10^4y	10^4z	10^4U_{11}[b]	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
					Anion				
Fe(1)	1160.7 (9)	1340.2 (9)	2077.4 (4)	540 (7)	655 (8)	542 (7)	112 (6)	−23 (4)	−104 (6)
C(1)	794 (8)	2716 (9)	1833 (4)	822 (59)	1031 (78)	783 (60)	128 (57)	157 (45)	−101 (56)
O(1)	491 (8)	3638 (7)	1690 (3)	1840 (75)	878 (51)	1352 (61)	542 (54)	311 (51)	56 (48)
C(2)	1526 (8)	−145 (10)	2251 (3)	796 (59)	1373 (92)	588 (56)	229 (60)	55 (41)	253 (56)
O(2)	1760 (8)	−1078 (7)	2346 (3)	1792 (74)	1068 (58)	1119 (54)	532 (53)	92 (47)	567 (47)
C(3)	−366 (8)	1161 (8)	2341 (3)	800 (60)	1079 (74)	696 (54)	125 (55)	9 (42)	−150 (52)
O(3)	−1343 (6)	1044 (8)	2512 (3)	670 (40)	1876 (81)	1545 (65)	−29 (47)	351 (41)	−53 (59)
C(4)	2165 (8)	1911 (9)	2585 (3)	809 (60)	1375 (88)	948 (68)	−8 (58)	−149 (49)	−430 (63)
O(4)	2817 (7)	2306 (8)	2913 (3)	1261 (58)	2224 (94)	1353 (61)	23 (61)	−461 (48)	−869 (65)
B(1)	1916 (7)	829 (7)	663 (3)	589 (48)	475 (45)	624 (51)	102 (39)	−35 (39)	−4 (40)
B(2)	3038 (7)	1848 (7)	817 (3)	520 (47)	595 (52)	676 (55)	28 (40)	62 (39)	−17 (44)
B(3)	2443 (7)	936 (7)	1377 (3)	493 (43)	536 (50)	575 (48)	108 (36)	41 (35)	−106 (38)
B(4)	873 (7)	635 (7)	1228 (3)	552 (46)	530 (50)	626 (52)	−35 (39)	−10 (38)	−128 (42)
B(5)	472 (7)	1436 (8)	566 (4)	519 (44)	721 (58)	677 (52)	12 (46)	−109 (38)	80 (50)
B(6)	1813 (8)	2251 (7)	395 (3)	654 (53)	522 (52)	723 (59)	3 (42)	29 (43)	−62 (45)
B(7)	2765 (10)	3422 (9)	711 (5)	857 (67)	711 (71)	1173 (86)	−290 (55)	273 (60)	−304 (61)
					Cation				
N(1)	3605 (4)	7135 (4)	795 (2)	399 (27)	316 (27)	691 (35)	22 (22)	40 (24)	−76 (25)
C(11)[a]	4299 (5)	8270 (5)	835 (3)	435 (33)	429 (36)	603 (41)	−9 (28)	−39 (29)	−66 (31)
C(12)	5674 (6)	8242 (6)	812 (3)	482 (36)	514 (39)	503 (39)	−55 (31)	8 (28)	62 (31)
C(13)	6186 (7)	9437 (7)	833 (4)	510 (44)	710 (55)	1155 (69)	−143 (40)	−34 (43)	−68 (50)
C(14)	7532 (7)	9534 (7)	976 (4)	577 (46)	752 (54)	967 (61)	−156 (40)	−10 (41)	−125 (47)
C(21)	3773 (6)	6602 (5)	221 (3)	544 (39)	390 (41)	896 (53)	−42 (31)	32 (36)	−126 (36)
C(22)	3286 (6)	7239 (7)	−284 (3)	633 (45)	692 (50)	716 (50)	−84 (40)	14 (37)	−67 (43)
C(23)	3489 (8)	6511 (9)	−813 (4)	873 (61)	1133 (80)	980 (70)	−199 (58)	−129 (51)	−285 (64)
C(24)	3021 (13)	7095 (14)	−1331 (6)	1537 (93)	2094 (95)	1220 (91)	−363 (95)	−124 (86)	−415 (92)
C(31)	2258 (5)	7418 (5)	911 (3)	439 (36)	430 (38)	751 (46)	38 (31)	16 (31)	−20 (34)
C(32)	1352 (6)	6429 (6)	864 (3)	558 (40)	524 (43)	900 (52)	−95 (37)	−14 (35)	90 (42)
C(33)	71 (6)	6831 (7)	1009 (3)	461 (39)	790 (53)	810 (52)	−109 (37)	−65 (34)	133 (43)
C(34)	−890 (7)	5923 (8)	937 (4)	559 (47)	1029 (70)	1348 (78)	−124 (46)	−67 (48)	402 (61)
C(41)	4114 (6)	6277 (6)	1215 (3)	448 (36)	435 (38)	1073 (60)	9 (34)	12 (35)	105 (43)
C(42)	4078 (7)	6592 (8)	1827 (4)	669 (49)	1122 (76)	875 (62)	−42 (49)	110 (42)	258 (56)
C(43)	4682 (12)	5616 (17)	2186 (7)	1211 (99)	2499 (92)	1338 (96)	303 (109)	−13 (81)	1159 (97)
C(441)	4531 (63)	5316 (54)	2662 (33)	936 (263)	1308 (311)	1364 (345)	−550 (358)	−335 (240)	810 (362)
C(442)	4643 (68)	5937 (53)	2732 (30)	1235 (240)	1604 (386)	865 (293)	−456 (301)	−140 (227)	833 (397)
C(443)	4155 (30)	4638 (25)	2319 (15)	1155 (237)	643 (181)	961 (220)	−249 (165)	−339 (188)	470 (173)

[a] *n*-Butyl chains are designated as C(*ij*): *i* = label for an individual *n*-butyl chain; *j* = position in relation to central nitrogen atom. [b] The complete temperature factor expression is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.



$$B_6H_{10} + NH_3 \rightarrow NH_4^+B_6H_9^- \qquad (1)$$

$$B_6H_{10} + HCl + BCl_3 \rightarrow B_6H_{11}^+BCl_4^- \qquad (2)$$

base through addition of a proton to the basal boron–boron bond to form $B_6H_{11}^+$. The basic character of B_6H_{10} is further exemplified by the insertion into the basal boron–boron bond of low-valent transition metals in electrophillic groups.[4] Of

$$B_6H_{10} + Fe_2(CO)_9 \rightarrow Fe(CO)_4B_6H_{10} + Fe(CO)_5 \qquad (3)$$

particular interest to the present investigation is the reaction which was first reported by Davison, Traficante, and Wreford (eq 3). In a preliminary[5] report, we described the derivative chemistry of $Fe(CO)_4B_6H_{10}$ which in part is given by reactions 4–6. A preliminary report[5] of the structure of $[N(n\text{-}C_4H_9)]^+[Fe(CO)_4B_7H_{12}]^-$ was also given at that time. We describe here the details of this structure.

$$Fe(CO)_4B_6H_{10} + KH \rightarrow K^+[Fe(CO)_4B_6H_9]^- + H_2 \qquad (4)$$

$$\begin{aligned} &K^+Fe(CO)_4B_6H_9^- + N(n\text{-}C_4H_9)_4I \\ &\quad \rightarrow [N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_6H_9]^- + KI \qquad (5) \end{aligned}$$

$$\begin{aligned} &N(n\text{-}C_4H_9)_4^+Fe(CO)_4B_6H_9^- + {}^1/_2\,B_2H_6 \\ &\quad \rightarrow [N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^- \qquad (6) \end{aligned}$$

Experimental Section

The preparation of $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$ was carried out according to reactions 3–6. The procedure for reaction 3 is essentially that reported earlier.[4,6] The procedures for reactions 4–6 are the same as those employed in the preparation of $B_6H_9^-$[6] and $B_7H_{12}^-$[7] salts.

Crystals of $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$ were grown from CH_2Cl_2 solution at −78 °C into which pentane was slowly diffused. The crystals were deep amber in color. They were sensitive to oxygen and moisture and decomposed at room temperature. Crystals were loaded into thin-walled glass capillaries under dry N_2 in a glovebox. The crystals proved to be very brittle and fractured easily when they were loaded into the capillaries. Only two crystals of adequate quality for data collection were found among the 50 crystals which were surveyed. The original report[5] of the structure of $[N(n\text{-}C_4H_9)_4]^+$-$[Fe(CO)_4B_7H_{12}]^-$ was based upon data obtained from one of these crystals. The results of the present study are based upon data obtained from the second crystal. The structures derived from the two data sets are in good agreement, but the second crystal underwent less decomposition than the first crystal. This yielded data from which smaller conventional and weighted *R* factors were calculated than from the first crystal.

The crystal used for the present study had approximate dimensions of 0.30 × 0.36 × 0.70 mm. Intensity data were collected at −70 °C. The cell dimensions and an orientation matrix for data collection were determined by least-squares refinement of 15 reflections, well centered on a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation (λ 0.7107 Å) monochromatized by reflection from an oriented graphite monochromator ($2\theta_{\text{mon}} = 11.69°$). Lattice parameters are $a = 10.840$ (5) Å, $b = 11.629$ (6) Å, $c = 23.698$ (10) Å, and $\beta = 90.15$ (3)°. The unit cell is monoclinic. The systematic extinctions ($h0l$, $l \neq 2n$; $0k0$,

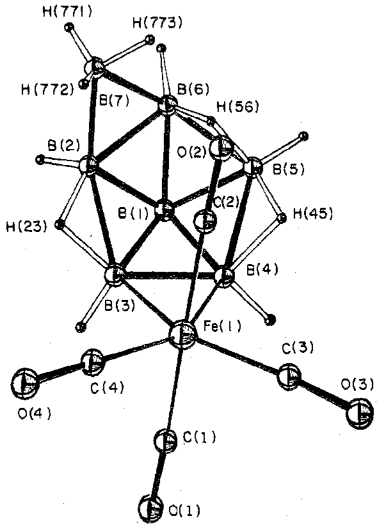


Figure 1. Plan view of $Fe(CO)_4B_7H_{12}^-$ (ORTEP plot using isotropic thermal parameters).

$k \neq 2n$) uniquely defined the space group as $P2_1/c$. An assumed $Z = 4$ gave $d_{calcd} = 1.10$ g/cm^3.

Data were collected using the θ–2θ scan mode ($2\theta_{max} = 50°$), and the reflections were scanned at a variable scan speed of 2–3°/min, depending upon intensity. The intensities of four standard reflections (006, 400, 11$\bar{2}$, and 30$\bar{4}$) were measured after every 100 intensity measurements. The crystal exhibited a constant decrease in intensity during the entire data collection, reaching a total of 12%. A linear correction as a function of time was applied to minimize the effect of the decomposition in the refinement. The intensity data were corrected for Lorentz and polarization effects, but absorption corrections were neglected since the calculated value of the linear absorption coefficient, μ, for Mo Kα radiation is 5.5 cm^{-1}. Of the 6432 reflections which were measured, 5980 were independent and 2685 for which $I \geq 3\sigma(I)$ were considered observed.

The structure was solved by the Patterson and Fourier techniques.[8] The atomic scattering factors used for Fe, O, N, C, and B were the values of Cromer and Waber,[9] and the atomic scattering factors for hydrogen were obtained from the calculation of Simpson, Davidson, and Stewart.[10] The quantity minimized in least-squares calculations was $w(|F_o| - |F_c|)^2$.

A trial position for the iron atom was obtained from a three-dimensional Patterson summation. Least-squares refinement of coordinates and an isotropic temperature factor gave a conventional R of 0.43. A Fourier map was then calculated which established the location of all remaining nonhydrogen atoms except the carbon atom of a disordered terminal methyl group. Refinement of all nonhydrogen atoms with isotropic temperature factors gave $R = 0.13$. Conversion to anisotropic temperature factors followed by three cycles of refinement reduced R to 0.12. A difference electron density synthesis revealed the positions of all but five of the hydrogen atoms and approximate positions for the disordered methyl carbon of the cation. The hydrogen atoms which could not be located were the terminal ethyl hydrogens of this disordered arm. In all subsequent refinements, the positional but not the thermal parameters of hydrogen were allowed to vary along with the positional and anisotropic thermal parameters of the heavier atoms.

For the final least-squares refinements, data were weighted by the function $w = 1/\sigma^2$, where $\sigma = 1.52 - 0.0032|F_o|$ for $|F_o| < 37.0$ and $\sigma = 0.30 + 0.0300|F_o|$ for $|F_o| \geq 37.0$, and corrections for anomalous dispersion[11] were applied to the scattering factors for iron ($\Delta f' = 0.37$, $\Delta f'' = 0.92$). Block-diagonal least-squares refinement converged with $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum(w|F_o| - |F_c|)^2/\sum w/F_o^2)^{1/2}$ equal to 0.068 and 0.075, respectively. Refinement was terminated when the shifts in all parameters were less than one-tenth of the estimated standard deviations. The error in an observation of unit weight, Σ, was $\Sigma = 1.30$.

Results and Discussion

Positional and anisotropic thermal parameters of nonhydrogen atoms are listed in Table I, while positional and isotropic thermal parameters of hydrogen are listed in Table II. Tables III, IV, V, and VI contain selected bond distances and bond angles for $Fe(CO)_4B_7H_{12}^-$ and $N(n\text{-}C_4H_9)_4^+$, respectively. No abnormally short nonbonded contact distances are observed between ions. The distances between nonbonded, nonhydrogen atoms all exceed 3.8 Å. Figures 1 and 2 are a

Table II. Coordinates and Isotropic Thermal Parameters for Hydrogen Atoms of $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$

Atom	10^3x	10^3y	10^3z	U
		Anion		
H(11)	217 (5)	13 (5)	39 (2)	0.060
H(22)	388 (5)	167 (5)	62 (2)	0.054
H(33)	311 (5)	24 (5)	150 (2)	0.063
H(44)	33 (5)	−25 (5)	122 (2)	0.070
H(55)	−27 (6)	120 (5)	25 (2)	0.066
H(66)	185 (5)	227 (5)	−9 (2)	0.064
H(771)	346 (6)	373 (6)	41 (3)	0.095
H(772)	276 (6)	370 (6)	117 (3)	0.095
H(773)	192 (7)	366 (6)	55 (3)	0.095
H(23)	295 (5)	203 (5)	138 (2)	0.059
H(45)	19 (5)	161 (5)	108 (2)	0.066
H(56)	55 (6)	265 (5)	55 (2)	0.068
		Cation		
H(111)	403 (5)	852 (5)	114 (2)	0.046
H(112)	403 (5)	874 (5)	58 (2)	0.046
H(121)	600 (5)	784 (5)	111 (2)	0.053
H(122)	588 (5)	806 (5)	47 (2)	0.053
H(131)	583 (6)	977 (6)	115 (3)	0.078
H(132)	597 (6)	986 (6)	58 (3)	0.078
H(141)	798 (6)	908 (6)	71 (3)	0.075
H(142)	777 (6)	899 (6)	130 (3)	0.075
H(143)	783 (6)	1012 (6)	99 (3)	0.075
H(211)	469 (5)	647 (5)	18 (2)	0.062
H(212)	344 (5)	590 (5)	18 (2)	0.062
H(221)	358 (6)	801 (6)	−34 (3)	0.073
H(222)	251 (6)	746 (6)	−21 (3)	0.073
H(231)	434 (7)	635 (7)	−83 (3)	0.101
H(232)	300 (7)	575 (7)	−79 (3)	0.101
H(241)	312 (7)	668 (7)	−164 (3)	0.104
H(242)	212 (7)	680 (7)	−135 (3)	0.104
H(243)	353 (7)	762 (7)	−137 (3)	0.104
H(311)	199 (5)	794 (5)	65 (2)	0.058
H(312)	228 (5)	778 (5)	129 (2)	0.058
H(321)	154 (5)	589 (5)	109 (3)	0.068
H(322)	139 (5)	614 (5)	50 (3)	0.068
H(331)	−2 (5)	737 (5)	75 (3)	0.066
H(332)	2 (6)	711 (6)	133 (3)	0.066
H(341)	−89 (7)	570 (7)	54 (3)	0.094
H(342)	−84 (7)	544 (7)	122 (3)	0.094
H(343)	−160 (7)	624 (7)	102 (3)	0.094
H(411)	494 (6)	613 (5)	107 (2)	0.065
H(412)	370 (5)	570 (5)	116 (2)	0.065
H(421)	454 (6)	712 (6)	191 (3)	0.086
H(422)	333 (6)	676 (6)	198 (3)	0.086

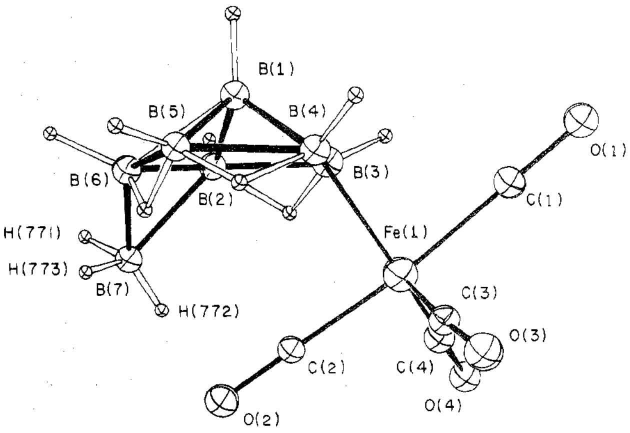


Figure 2. Profile view of $Fe(CO)_4B_7H_{12}^-$ (ORTEP plot using isotropic thermal parameters).

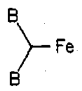
Table III. Bond Distances and Standard Deviations for the $[Fe(CO)_4B_7H_{12}]^-$ Anion

Atoms	Distance, A	Atoms	Distance, A	Atoms	Distance, A
Fe(1)-B(3)	2.218 (8)	Fe(1)-B(4)	2.196 (8)	Fe(1)-C(1)	1.747 (11)
Fe(1)-C(2)	1.819 (12)	Fe(1)-C(3)	1.783 (9)	Fe(1)-C(4)	1.752 (9)
C(1)-O(1)	1.171 (13)	C(2)-O(2)	1.137 (14)	C(3)-O(3)	1.142 (11)
C(4)-O(4)	1.145 (12)	B(1)-B(2)	1.735 (12)	B(1)-B(3)	1.788 (11)
B(1)-B(4)	1.769 (12)	B(1)-B(5)	1.732 (11)	B(1)-B(6)	1.775 (12)
B(2)-B(3)	1.819 (12)	B(2)-B(6)	1.725 (12)	B(2)-B(7)	1.871 (14)
B(3)-B(4)	1.773 (11)	B(4)-B(5)	1.874 (12)	B(5)-B(6)	1.783 (12)
B(6)-B(7)	1.864 (14)	B(1)-H(11)	1.08 (6)	B(2)-H(22)	1.05 (6)
B(2)-H(23)	1.36 (6)	B(3)-H(23)	1.38 (6)	B(3)-H(33)	1.12 (6)
B(4)-H(44)	1.18 (6)	B(4)-H(45)	1.40 (6)	B(5)-H(45)	1.26 (6)
B(5)-H(55)	1.14 (6)	B(5)-H(56)	1.41 (6)	B(6)-H(56)	1.49 (6)
B(6)-H(66)	1.14 (6)	B(7)-H(771)	1.10 (7)	B(7)-H(772)	1.14 (7)
B(7)-H(773)	1.03 (7)				

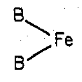
Table IV. Bond Angles and Standard Deviations for the $[Fe(CO)_4B_7H_{12}]^-$ Anion

Atoms	Angles, deg	Atoms	Angles, deg
B(3)-Fe(1)-B(4)	47.4 (3)	B(3)-Fe(1)-C(1)	95.1 (4)
B(3)-Fe(1)-C(2)	80.3 (3)	B(3)-Fe(1)-C(3)	145.2 (3)
B(3)-Fe(1)-C(4)	101.8 (4)	B(4)-Fe(1)-C(1)	90.4 (4)
B(4)-Fe(1)-C(2)	83.3 (3)	B(4)-Fe(1)-C(3)	98.5 (3)
B(4)-Fe(1)-C(4)	149.1 (4)	C(1)-Fe(1)-C(2)	173.7 (4)
C(1)-Fe(1)-C(3)	90.7 (4)	C(1)-Fe(1)-C(4)	91.2 (5)
C(2)-Fe(1)-C(3)	90.6 (4)	C(2)-Fe(1)-C(4)	94.0 (4)
C(3)-Fe(1)-C(4)	112.3 (4)	Fe(1)-B(3)-B(1)	121.6 (5)
Fe(1)-B(3)-B(2)	130.3 (5)	Fe(1)-B(3)-B(4)	65.7 (4)
Fe(1)-B(4)-B(1)	123.8 (5)	Fe(1)-B(4)-B(3)	67.0 (4)
Fe(1)-B(4)-B(5)	127.8 (5)	Fe(1)-C(1)-O(1)	176.1 (8)
Fe(1)-C(2)-O(2)	178.3 (9)	Fe(1)-C(3)-O(3)	179.8 (9)
Fe(1)-C(4)-O(4)	178.6 (9)	B(2)-B(1)-B(3)	62.1 (5)
B(2)-B(1)-B(4)	112.2 (6)	B(2)-B(1)-B(5)	112.5 (6)
B(2)-B(1)-B(6)	58.8 (5)	B(3)-B(1)-B(4)	59.8 (4)
B(3)-B(1)-B(5)	112.6 (6)	B(3)-B(1)-B(6)	107.1 (6)
B(4)-B(1)-B(5)	64.7 (5)	B(4)-B(1)-B(6)	110.5 (6)
B(5)-B(1)-B(6)	61.1 (5)	B(1)-B(2)-B(3)	60.4 (5)
B(1)-B(2)-B(6)	61.7 (5)	B(1)-B(2)-B(7)	121.9 (6)
B(3)-B(2)-B(6)	107.9 (6)	B(3)-B(2)-B(7)	127.8 (6)
B(6)-B(2)-B(7)	62.3 (5)	B(1)-B(3)-B(2)	57.5 (4)
B(1)-B(3)-B(4)	59.6 (4)	B(2)-B(3)-B(4)	108.2 (5)
B(1)-B(4)-B(3)	60.7 (4)	B(1)-B(4)-B(5)	56.7 (4)
B(3)-B(4)-B(5)	106.8 (5)	B(1)-B(5)-B(4)	58.6 (4)
B(1)-B(5)-B(6)	60.6 (5)	B(4)-B(5)-B(6)	105.5 (5)
B(1)-B(6)-B(2)	59.4 (5)	B(1)-B(6)-B(5)	58.3 (5)
B(1)-B(6)-B(7)	120.2 (6)	B(2)-B(6)-B(5)	110.5 (6)
B(2)-B(6)-B(7)	62.7 (5)	B(5)-B(6)-B(7)	138.4 (7)
B(2)-B(7)-B(6)	55.0 (5)		

plan view and a profile view of the $Fe(CO)_4B_7H_{12}^-$ ion, respectively. The structure is essentially a pentagonal-pyramidal B_6H_9 unit into which has been inserted an $Fe(CO)_4$ group and a BH_3 group in nonadjacent bridging sites. Bonding of the iron to the B_6H_9 group can be represented in terms of two possible valence bond representations. In representation I the



I



II

iron is formally dsp^3 hybridized with a closed two-electron three-center B–Fe–B bond formed through the donation of the electron pair in a basal boron–boron bond to the vacant dsp^3 orbital of iron. This arrangement is analogous to the representation of the donation of the electron pair in the π molecular orbital of an olefin to a vacant hybrid orbital of a metal.[12] Representation II involves the iron being formally d^2sp^3 hybridized. The bonding involves two two-center Fe–B bonds each involving interaction of an sp^3 orbital of boron with a d^2sp^3 orbital of iron with boron and iron each supplying an electron to each bond. Infrared and Mössbauer spectral data have been used to infer bonding situation I in the case of $Fe(CO)_4B_6H_{10}$.[4a] In the present case the structural data also favor I since the B(3)–B(4) distance, 1.773 (11) Å, is consistent with a bonding situation. If structure II were operative this distance would be significantly longer since these atoms would not participate in a common bond. Furthermore, the observed C(3)–Fe(1)–C(4) angle for equatorial CO groups (112.3 (4)°) is closer to the ideal value for dsp^3 hybridization (120°) than for d^2sp^3 (90°). Repulsion from B(3) and B(4) and their associated H atoms probably account for the smaller than ideal bond angle. Figure 1 shows a coordination sphere around the iron which can be interpreted as a trigonal bipyramid with the four carbons serving as four vertices and the center of the B(3)–B(4) bond serving as the fifth vertex. All of the C–Fe–C angles are consistent with this representation. The distances Fe–B(3), 2.218 (8) Å, and Fe–B(4), 2.196 (8) Å, are somewhat longer than the Fe–B single bond distance of 1.975 Å which is predicted from Pauling's single bond radii.[13] These "long" distances are consistent with three-center B–Fe–B bonding whereby the individual Fe–B interactions, if treated as separate bonds, would have fractional bond orders less than one. Possible Fe–H–B bonding as an alternative or supplement to B–Fe–B bonding seems remote since the Fe–H distances of 2.82 (5) and 2.89 (6) Å with respect to terminal hydrogens on B(3) and B(4) are significantly longer than the Fe–H distances (ca. 1.8 Å) observed in Fe–H–Fe bridging situations.[14]

Atoms B(3), B(4), C(3), and C(4) define a plane with Fe being 0.05 Å above the plane. The dihedral angle between this plane and that defined by the basal borons B(2), B(3), B(4), B(5), and B(6) is 124°.

Within the B_6H_9 framework, the boron–boron distances and boron–hydrogen distances fall within the ranges of values previously reported for boron hydrides. The apical boron lies 0.88 Å above the plane of the five basal boron atoms. At the coordination site of the $Fe(CO)_4$ group the B(3)–B(4) distance is 1.773 (11) Å. The coordination site before addition of $Fe(CO)_4$ was 1.60 (1) Å in length; this is the basal B–B bond

Table V. Bond Distances and Standard Deviations for Nonhydrogen Atoms in the Tetra-*n*-butylammonium Cation

Atoms	Distance, A	Atoms	Distance, A	Atoms	Distance, A
N(1)-C(11)	1.522 (8)	N(1)-C(21)	1.507 (9)	N(1)-C(31)	1.522 (7)
N(1)-C(41)	1.513 (9)	C(11)-C(12)	1.492 (8)	C(12)-C(13)	1.497 (10)
C(13)-C(14)	1.501 (10)	C(21)-C(22)	1.501 (11)	C(22)-C(23)	1.529 (13)
C(23)-C(24)	1.491 (17)	C(31)-C(32)	1.517 (9)	C(32)-C(33)	1.506 (9)
C(33)-C(34)	1.492 (11)	C(41)-C(42)	1.496 (12)	C(42)-C(43)	1.561 (20)
C(43)-C(441)	1.194 (78)	C(43)-C(442)	1.348 (65)	C(43)-C(443)	1.311 (35)

Table VI. Bond Angles and Standard Deviations for Nonhydrogen Atoms in the Tetra-*n*-butylammonium Cation

Atoms	Angle, deg	Atoms	Angle, deg
C(11)-N(1)-C(21)	110.6 (5)	C(11)-N(1)-C(31)	106.0 (4)
C(11)-N(1)-C(41)	110.6 (4)	C(21)-N(1)-C(31)	111.7 (5)
C(21)-N(1)-C(41)	106.2 (5)	C(31)-N(1)-C(41)	111.9 (5)
N(1)-C(11)-C(12)	118.2 (5)	C(11)-C(12)-C(13)	110.5 (5)
C(12)-C(13)-C(14)	116.0 (6)	N(1)-C(21)-C(22)	118.2 (5)
C(21)-C(22)-C(23)	109.2 (7)	C(22)-C(23)-C(24)	112.0 (9)
N(1)-C(31)-C(32)	116.4 (5)	C(31)-C(32)-C(33)	110.2 (6)
C(32)-C(33)-C(34)	113.5 (7)	N(1)-C(41)-C(42)	117.8 (6)
C(41)-C(42)-C(43)	109.8 (9)	C(42)-C(43)-C(441)	132 (3)
C(42)-C(43)-C(442)	108 (3)	C(42)-C(43)-C(443)	125 (2)

length in B_6H_{10}.[15] Opening of this bond by insertion of a metal atom has also been observed in the case of $Cl_2Pt(B_6H_9)_2$ (1.79 (2) Å).[4c] The $B_6H_9^-$ ion has two basal B–B bonds. In the molecule $Mg(C_4H_8O)_2(B_6H_9)_2$ one of these sites is occupied by Mg(1.679 (14) Å).[16] The remaining B–B site is 1.603 (18) Å long and occupies a position which corresponds to the B–B site in $Fe(CO)_4B_6H_9^-$. At the coordination site of the BH_3 group in $Fe(CO)_4B_6H_9^-$ the B(2)–B(6) distance is 1.725 (12) Å. It seems likely that addition of BH_3 to $Fe(CO)_4B_6H_9^-$ opens the B–B bond.

At the coordination site of BH_3 the B(2)–B(7) and the B(6)–B(7) distances are 1.871 (14) and 1.864 (14) Å. One of the hydrogens H(773) of the inserted BH_3 group occupies a position which suggests possible bridging to B(6) on the B_6H_9 framework. While the H(773)–B(6) distance of 1.68 (8) Å is significantly larger than the generally observed B–H distance of 1.3 Å in a B–H–B bond, it is noteworthy that in B_5H_{11} one of the apical hydrogens is oriented in a bridging position with respect to the two outer basal borons.[17] Not only is one hydrogen of the BH_3 group in $Fe(CO)_4B_4H_{12}^-$ in a "pseudo" bridging position but there also appears to be significant distortion of the BH_3 group such that it might be considered as a BH_2 group with the third hydrogen being the "pseudo" bridging hydrogen. Thus consistent with a BH_2 group an H(771)–B(7)–H(772) angle of 122 (5)° is observed and the dihedral angle between the plane defined by H(771), B(7), and H(772) and the plane defined by B(2), B(6), and B(7) is 80°. The H(771)–B(7)–H(773) and H(772)–B(7)–H(773) bond angles are 106 (5)°.

The three ordered branches of the $N(n\text{-}C_4H_9)_4^+$ group have the trans conformation. The δ carbon of the fourth branch is badly disordered, a common feature of the $N(n\text{-}C_4H_9)_4^+$ ion,[19] and all attempts to obtain accurate positions were fruitless. The average N–C bond length is 1.511 (8) Å. Excluding the disordered methyl group, the range of the C–C bond lengths is 1.492 (8)–1.561 (20) Å, with an average value of 1.512 Å. The bond angles in the *n*-butyl chains have the following average values: $C\alpha\text{–}N\text{–}C\alpha = 108.9\ (4)°$; $N\text{–}C\alpha\text{–}C\beta = 117.6\ (5)°$; $C\alpha\text{–}C\beta\text{–}C\gamma = 109.9\ (5)°$; $C\beta\text{–}C\gamma\text{–}C\delta = 113.8\ (7)°$. Two of the ordered chains have dihedral angles which are close to 0°, showing planarity. The mean C–H bond distance for the cation is 0.91 (6) Å as estimated by $\bar{\chi} = \sum_i(\chi_i/\sigma_i^2)(\sum_i(1/\sigma_i^2)$.

Plane defined by atoms	Plane defined by atoms	Dihedral angle, deg
C(11) C(12) C(13)	C(12) C(13) C(14)	16.5
C(21) C(22) C(23)	C(22) C(23) C(24)	0.2
C(31) C(32) C(33)	C(32) C(33) C(34)	3.6

Acknowledgment. We wish to thank the National Science Foundation for support of this work. W.R.C. thanks The Ohio State University Graduate School for a Postdoctoral Fellowship.

Registry No. $[N(n\text{-}C_4H_9)_4]^+[Fe(CO)_4B_7H_{12}]^-$, 54083-17-9.

Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1972.
(2) (a) G. L. Brubaker, M. L. Denniston, S. G. Shore, J. C. Carter, and F. Swicker, *J. Am. Chem. Soc.*, **92**, 7216 (1970); (b) H. D. Johnson, II, S. G. Shore, N. L. Mock, and J. C. Carter, *ibid.*, **91**, 2131 (1969); (c) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, **9**, 908 (1970).
(3) (a) H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Am. Chem. Soc.*, **94**, 6711 (1972); (b) J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, **9**, 2157 (1970); (c) J. J. Solomon and R. F. Porter, *J. Am. Chem. Soc.*, **94**, 1443 (1972).
(4) (a) A. Davison, D. D. Traficante, and S. S. Wreford, *J. Am. Chem. Soc.*, **96**, 2802 (1974); (b) *J. Chem. Soc., Chem. Commun.*, 1155 (1972); (c) J. P. Brennan, R. Schaeffer, A. Davison, and S. S. Wreford, *ibid.*, 354 (1973).
(5) O. Hollander, W. R. Clayton, and S. G. Shore, *J. Chem. Soc., Chem. Commun.*, 604 (1974).
(6) V. T. Brice, H. D. Johnson, II, D. L. Denton, and S. G. Shore, *Inorg. Chem.*, **11**, 1135 (1972).
(7) R. J. Remmel, H. D. Johnson, II, I. S. Jaworiwsky, and S. G. Shore, *J. Am. Chem. Soc.*, **97**, 5305 (1975).
(8) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, "The X-ray Ststem", Technical Report TR-192, June, 1972, Computer Science Center, University of Maryland, College Park, Md.
(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(11) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(12) F. A. Cotton and G. Wilkenson, "Advanced Inorganic Chemistry", Interscience, New York, N.Y., 1972, p 730.
(13) L. C. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, p 256.
(14) R. Bau, B. Don, R. Greatrex, R. J. Haines, R. A. Love, and R. D. Wilson, *Inorg. Chem.*, **14**, 3021 (1975).
(15) (a) F. L. Hirshfeld, K. Ericks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958); (b) J. C. Huffman, *Diss. Abstr. B*, **35**, 2118 (1974).
(16) D. L. Denton, W. R. Clayton, M. Mangion, S. G. Shore, and E. A. Meyers, *Inorg. Chem.*, **15**, 541 (1976).
(17) (a) L. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 614 (1954); (b) J. C. Huffman, Ph.D. Thesis, Indiana University, 1974.
(18) R. R. Rietz, R. Schaeffer, and L. G. Sneddon, *J. Am. Chem. Soc.*, **92**, 3514 (1970).
(19) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973).