Registry No. Bis(dibutylphosphinato)copper(II), 58281-35-9.

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Structure of an Iron(II) Complex with a Novel Sexadentate Ligand Derived from a Tetraaza Macrocycle

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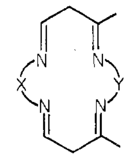
Recent investigations of a series of low-spin iron(II) complexes with macrocyclic ligands have yielded a new sexadentate iron(II) chelate formed by the electrophilic attack of two coordinated acetonitrile molecules at the apical carbons of the parent macrocycles. In this way the acetonitriles form appended iminoethyl groups that are well oriented for chelation. A three-dimensional x-ray crystallographic structural determination has confirmed and clarified the unique nature of the complex. *cis*-3,11-Bis(1-iminoethyl-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraeneiron(II) hexafluorophosphate crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 21.647$ (19), $b = 11.077$ (11), and $c = 11.115$ (9) Å. The structure was solved by Fourier and least-squares techniques to a conventional $R = 0.064$ for 2787 reflections. The six nitrogens form a slightly trigonal distorted octahedron and the iron nitrogen distances vary from 1.936 to 1.971 Å. The average C–N bond length of 1.256 Å coincides with double bond localization in these rings. The coordination sphere therefore consists of six imine nitrogen donors. The macrocycle is folded and the nitrogens of the iminoethyl groups are coordinated in cis positions.

Introduction

Recent studies on the chemistry of complexes of synthetic macrocyclic ligands have tended to focus on those reactions which mimic the behavior of natural systems such as heme-iron proteins and on the changes in the chemical and physical properties which are attendant upon systematic variations in the structure of the ring. The former are well illustrated by the considerable progress in the development of oxygen-carrying chelates[1-3] while the latter include the dependence of redox properties[4,5] and ligand field strengths[6] on such structural parameters as ring size, extent and arrangement of unsaturated groups, and ligand charge. Structures derived from macrocyclic ligands that have been modified by appended groups are of increasing importance. The function of the metal ion in complicated natural molecules, such as heme proteins and vitamin B_{12}, is controlled in part by the extracyclic part of the structure. Studies on synthetic O_2 carriers have exploited this theme. Traylor and his associates appended an imidazole to a porphyrin ring;[2] Collman et al. produced a "picket fence" porphyrin,[3] and Baldwin and Huff provided a structure wherein a hydrophobic moiety shields one coordination site above a porphyrin.[1] Studies in these laboratories are directed toward the use of extracyclic groups to control the total environment about the metal atom in synthetic, nonporphyrin macrocycles. Earlier reports have included the attachment of a fifth donor atom so placed that it filled a coordination site and the appending of other functional and hydrophobic groups.[7] Cytochrome *c* exemplifies the case where the two coordination sites not filled by a tetradentate macrocyclic ligand are occupied by donor groups propitiously arrayed for chelation by the protein portion of a natural product. We report in a separate paper[8] the fortuitous synthesis and characterization of a series of complexes of the latter class. The structure of one of these is reported here.

Results and Discussion

When macrocycles of general structure I react with solvated ferrous iron in acetonitrile solution, complexes are formed that can be isolated as the hexafluorophosphate salts.[8] These salts uniformly have the composition of bis(acetonitrile) solvates, i.e., $Fe(MAC)(PF_6)_2 \cdot 2CH_3CN$. Only the 14-membered ring derivative, however, involves the most obvious possible structure wherein the macrocycle is coordinated in a planar fashion about the Fe^{2+} ion with the acetonitrile molecules coordinated at the two axial sites. Application of the usual physical and chemical methods of characterization to the bis(acetonitrile) adducts of the iron complexes with the 15- and 16-membered rings revealed disquieting chemical and physical properties. Most striking among the physical properties were the absence



Ia, $X = (CH_2)_2$; $Y = (CH_2)_2$
b, $X = (CH_2)_2$; $Y = (CH_2)_3$
c, $X = (CH_2)_3$; $Y = (CH_2)_3$

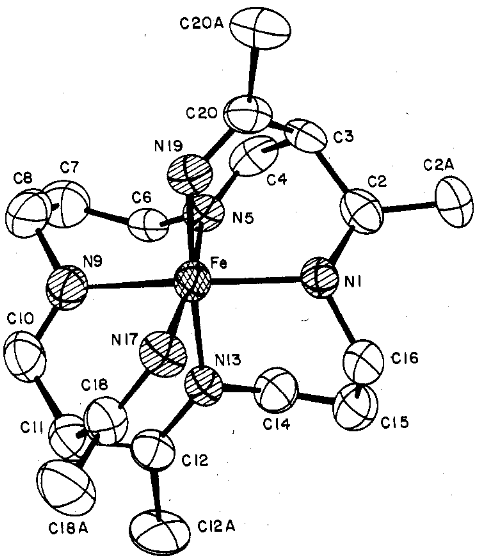
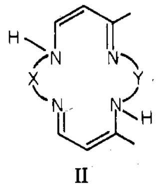


Figure 1. ORTEP plot of $[Fe(Me_2IE_2[16]tetraeneN_4)]^{2+}$. The thermal ellipsoids in this and Figure 3 are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

of the weak $-C{\equiv}N$ stretch often observed in the infrared spectra of acetonitrile complexes and the presence of an absorption that looked like an N—H stretching vibration at 3310 cm^{-1}, as well as related complexities in the NMR spectrum. Chemically the compounds were found to be remarkably inert toward bases. Whereas the difficulties in the physical properties could be explained away, at least in part, by assuming the tautomeric structure II for the macrocycle, it remained surprising that the low-spin six-coordinate complex containing this ligand could be caused to ionize its most acidic protons only with bases as strong as *tert*-butoxide ion. At this stage an x-ray crystallographic study was performed on one of the compounds, the derivative of ligand Ic, thereby revealing an unusual structure and a most interesting and novel ligand reaction as well.



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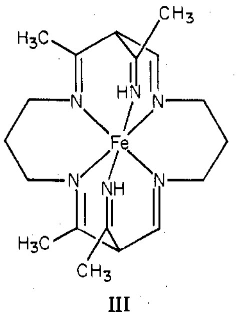

III

The product in question, *cis*-[3,11-bis(1-iminoethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraeneiron(II)] hexafluorophosphate (abbreviated $[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$, structure III) is formed by the condensation of acetonitrile with the 16-membered macrocycle of structure I, under the influence of the ferrous ion. The iron atom has the low-spin d^6 configuration and the salt exists as a 2:1 electrolyte in solution.[8] The formation of $[Fe(Me_2IE_2[16]tetraeneN_4)]^{2+}$ by this reaction is remarkable in view of the chemical properties of nitriles. This interesting process is discussed elsewhere.[8]

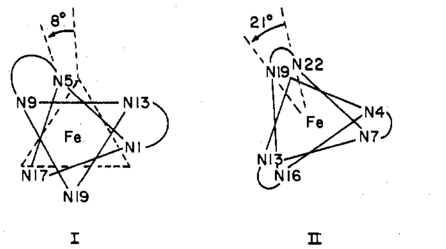

Figure 2. Trigonal distortion in $[Fe(Me_2IE_2[16]tetraeneN_4)]^{2+}$ (I) and in an iron(II) clathro chelate (ref 9) (II).

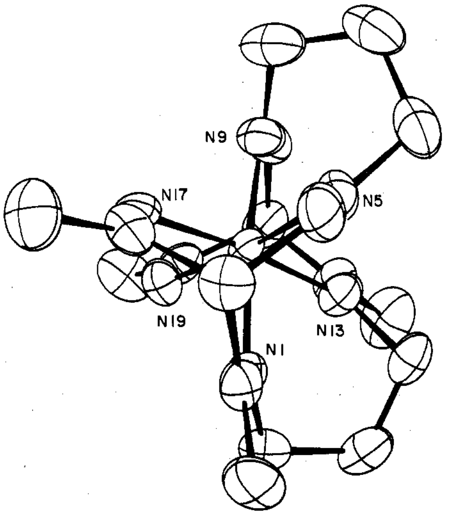

Figure 3. Perspective drawing of $[Fe(Me_2IE_2[16]tetraeneN_4)]^{2+}$ as viewed down an axis extending through the two bridgehead carbon atoms. Hydrogen atoms have been omitted for clarity.

Structure of $[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$

As shown in Figure 1, the coordination sphere of the iron atom consists of a somewhat distorted octahedral array of nitrogen atoms which can best be considered to result from a slight trigonal twist of 8° from ideal octahedral geometry. Similar findings have been observed by Goedken in a study of a sexadentate iron(II) clathro chelate;[9] however, the twist angle is much greater in that case (39°). These relationships are shown diagramatically in Figure 2. Additional interesting stereochemical aspects of the structure relate to the trigonal arrays of nitrogen donors radiating from common bridgehead carbon atoms. Each triangular array of imine nitrogens is essentially equilateral with the projected angles averaging 60.3 (5)°, and the bridgehead carbons of the parent macrocycle are situated above the approximate centers of the triangles.

Another interesting stereochemical feature is seen when the complex is viewed down an axis extending through the two bridgehead carbon atoms (Figures 2 and 3). Consider the two rings that correspond to the saturated trimethylene bridges. If, in thought, one replaces the two imino hydrogens on N17 and N19 (Figure 3) by a third trimethylene bridge, the molecule would approximate D_3 symmetry, as well as become a clathro chelate.

The bond lengths and angles are generally consistent with expectations (Tables I and II). The Fe–N bond distances are found to vary somewhat, ranging from 1.936 (5) to 1.971 (5) Å. As no alternate cause for this observation is evident, the variations can most probably be attributed to strain within the chelating ligand. While an Fe–N bond distance of 1.97 Å is predicted for low-spin iron(II) bound to six monodentate nitrogen donors on the basis of covalent radii, distances as short as 1.90 Å have been reported.[10,11] Hoard has suggested that

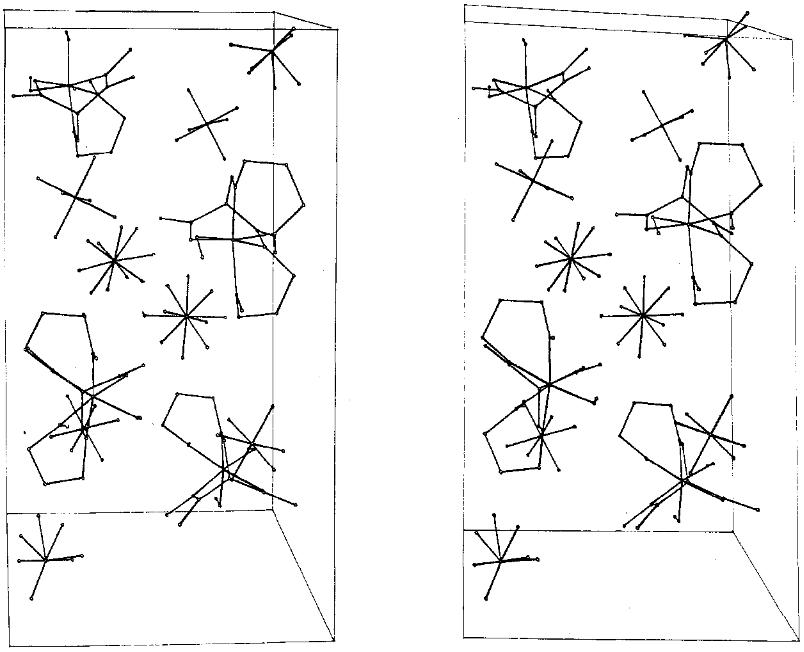

Figure 4. Packing diagram of $[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$ as viewed down the *c* axis.

Table I. Bond Angles[a] (deg)

N_1FeN_5	88.1 (2)	$C_8N_9C_{10}$	121.0 (6)
N_5FeN_9	87.5 (2)	$N_9C_{10}C_{11}$	119.2 (6)
N_9FeN_{13}	98.1 (2)	$C_{10}C_{11}C_{12}$	109.9 (6)
$N_{13}FeN_{17}$	178.9 (2)	$C_{11}C_{12}C_{12}A$	117.8 (6)
$N_{17}FeN_{19}$	89.7 (2)	$C_{11}C_{12}N_{13}$	114.8 (6)
$N_1C_2C_2A$	128.5 (6)	$C_{12}N_{13}C_{14}$	120.6 (6)
$N_1C_2C_3$	114.3 (5)	$N_{13}C_{14}C_{15}$	110.7 (6)
$C_2C_3C_4$	109.0 (6)	$C_{14}C_{15}C_{16}$	114.6 (6)
$C_3C_4N_5$	117.4 (6)	$C_{15}C_{16}N_1$	109.8 (6)
$C_4N_5C_6$	119.9 (6)	$N_{17}C_{18}C_{18}A$	125.4 (7)
$N_5C_6C_7$	111.7 (6)	$N_{19}C_{20}C_{20}A$	125.4 (7)
$C_6C_7C_8$	115.0 (6)	$C_2C_3C_{18}$	108.6 (6)
$C_7C_8N_9$	111.3 (7)	$C_{10}C_{11}C_{20}$	106.7 (6)

[a] Standard deviations are given in parentheses here and in Table II.

Table II. Bond Lengths (Å)

Fe-N_1	1.971 (5)	N_{13}-C_{14}	1.473 (9)
Fe-N_5	1.950 (6)	C_{14}-C_{15}	1.522 (11)
Fe-N_9	1.936 (5)	C_{15}-C_{16}	1.542 (11)
Fe-N_{13}	1.950 (6)	N_{17}-C_{18}	1.278 (8)
Fe-N_{17}	1.949 (6)	C_{18}-$C_{18}A$	1.485 (10)
Fe-N_{19}	1.969 (6)	N_{19}-C_{20}	1.257 (8)
N_1-C_2	1.289 (8)	C_{20}-$C_{20}A$	1.493 (10)
C_2-C_2A	1.493 (8)	P_1-F_1	1.547 (7)
C_2-C_3	1.542 (9)	P_1-F_2	1.591 (7)
C_3-C_4	1.520 (10)	P_1-F_3	1.551 (11)
C_3-C_{18}	1.513 (10)	P_1-F_4	1.568 (12)
C_4-N_5	1.270 (9)	P_1-F_5	1.541 (11)
N_5-C_6	1.466 (9)	P_1-F_6	1.572 (12)
C_6-C_7	1.534 (12)	P_1-F_3A	1.608 (22)
C_7-C_8	1.508 (12)	P_1-F_4A	1.672 (21)
C_8-N_9	1.479 (9)	P_1-F_5A	1.592 (23)
N_9-C_{10}	1.249 (9)	P_1-F_6A	1.662 (22)
C_{10}-C_{11}	1.490 (10)	P_2-F_7	1.587 (6)
C_{11}-C_{12}	1.526 (10)	P_2-F_8	1.583 (5)
C_{11}-C_{20}	1.541 (10)	P_2-F_9	1.562 (6)
C_{12}-$C_{12}A$	1.517 (10)	P_2-F_{10}	1.597 (6)
C_{12}-N_{13}	1.289 (8)	P_2-F_{11}	1.572 (6)
		P_2-F_{12}	1.587 (6)

the Fe–N bond length is influenced to a large extent both in metalloporphyrins and in synthetic metallomacrocyclic structures by the ligand framework[12] and should thus vary according to the identity of the macrocycle.

In the present structure, the two donor atoms associated with the iminoethyl branch chains are coordinated in cis positions. This is accompanied by folding of the parent macrocycle so that the binding of the four nitrogen donors of the ring is constrained by somewhat altered stereochemical relationships from those usually associated with macrocycles that are coordinated in a planar fashion. It appears reasonable to presume that the folded ring conformation offers less restriction on the metal nitrogen distances than would follow from the encompassing of the metal ion in the coplanar conformation in which macrocycles usually coordinate. The six C═N bonds in the unsaturated rings are localized as evidenced by the short C—N lengths averaging 1.256 (8) Å. Consequently, the coordination sphere consists of six isolated imine donors. Both of the saturated six-membered rings exhibit twist conformations.

Of the two PF_6 counterions, one was found to be disordered about a fourfold axis extending through two trans fluorines. This is evident in the packing diagram as viewed down the *c* axis in Figure 4. The disorder is best described as the result of a $\pi/4$ rotation about the axis with an occupancy factor ratio of 3:1 for the two configurations. A similar phenomenon was recently observed in the structure of $[Ru(NH_3)_6][PF_6]_2$[13] and was attributed to crystal packing effects.

Structure Determinations

A small crystal of the orange salt *cis*-[3,11-bis(1-iminoethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-iron(II)] hexafluorophosphate (0.25 × 0.40 × 0.50 mm) was mounted, and preliminary data were obtained from precession photographs using Mo Kα radiation. The crystal displayed orthorhombic symmetry with systematic absences at $h00$ ($h \neq 2n$), $0k0$ ($k \neq 2n$), and $00l$ ($l \neq 2n$), indicating the space group to be $P2_12_12_1$ (D_2^4, No. 19). Cell dimensions were determined on a Picker four-circle diffractometer from a least-squares fit of accurately measured angular settings for 16 reflections and are a = 21.647 (19) Å, b = 11.077 (11) Å, c = 11.115 (9) Å, and V = 2665.1 Å^3. The calculated density of 1.68 g/cm^3, on the basis of four molecules per unit cell, agrees with the observed density of 1.68 (1) g/cm^3 obtained by flotation in CCl_4/CH_3I. Intensity measurements were made on a Picker FACS III four-circle diffractometer controlled by an EMR 6130 computer. The θ–2θ scanning technique was used with a scan range of 2° centered on the calculated 2θ value for each reflection and a scan rate of 2°/min. Background counts of 10 s were made at the beginning and end of each scan. Zr-filtered Mo Kα radiation (λ No. 7107 Å) was employed with a takeoff angle of 2°. The intensities of three reflections, chosen

Table III. Fractional Coordinates and Thermal Motion Parameters[a] Derived from the Least-Squares Refinement for $[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$

Atom	x	y	z	10^5B_{11}	10^5B_{22}	10^5B_{33}	10^5B_{12}	10^5B_{13}	10^5B_{23}
Fe	0.13346 (4)	0.22387 (8)	0.24184 (7)						
P_1	0.4483 (1)	0.3746 (3)	0.3788 (2)	256 (5)	1256 (25)	824 (18)	−32 (10)	−101 (8)	97 (19)
P_2	0.2996 (1)	0.2201 (2)	0.7981 (2)	253 (5)	992 (20)	687 (14)	122 (9)	−50 (7)	−70 (17)
F_1	0.4235 (3)	0.2909 (10)	0.2784 (6)	493 (21)	4525 (172)	1797 (79)	−602 (51)	223 (33)	−1727 (109)
F_2	0.4730 (5)	0.4616 (8)	0.4821 (7)	1095 (42)	2000 (97)	1782 (81)	−455 (53)	−496 (52)	−500 (77)
F_3	0.4053 (5)	0.3148 (11)	0.4728 (10)	11.2 (3)					
F_4	0.4911 (6)	0.4264 (12)	0.2778 (12)	11.9 (3)					
F_5	0.5013 (5)	0.2932 (11)	0.4234 (10)	11.0 (3)					
F_6	0.3935 (5)	0.4563 (11)	0.3347 (11)	11.6 (3)					
F_3A	0.3802 (10)	0.3957 (21)	0.4341 (21)	6.3 (5)					
F_4A	0.5124 (9)	0.3582 (22)	0.2962 (19)	5.5 (4)					
F_5A	0.4567 (11)	0.2503 (21)	0.4487 (21)	6.8 (5)					
F_6A	0.4432 (10)	0.5154 (20)	0.3296 (20)	5.9 (4)					
F_7	0.2249 (3)	0.2824 (9)	0.7832 (6)	579 (22)	3748 (135)	1513 (67)	1076 (48)	−284 (31)	−675 (82)
F_8	0.3556 (2)	0.1559 (5)	0.8120 (6)	216 (11)	1348 (60)	2057 (69)	50 (20)	−109 (23)	52 (58)
F_9	0.2646 (2)	0.1043 (6)	0.7359 (6)	294 (12)	1516 (66)	2184 (77)	−101 (23)	41 (28)	−839 (66)
F_{10}	0.3177 (4)	0.3395 (5)	0.8583 (6)	820 (28)	1070 (60)	1574 (65)	−149 (34)	−126 (39)	−294 (57)
F_{11}	0.2706 (3)	0.1737 (6)	0.9257 (5)	508 (19)	202 (84)	1097 (49)	−112 (33)	74 (26)	344 (59)
F_{12}	0.3084 (4)	0.2735 (7)	0.6703 (5)	839 (28)	213 (86)	816 (43)	99 (46)	132 (30)	386 (59)
N_1	0.0489 (2)	0.2265 (5)	0.1760 (4)	148 (10)	608 (45)	607 (40)	28 (21)	−24 (17)	−115 (43)
C_2	0.0387 (3)	0.2234 (7)	0.0618 (5)	198 (14)	623 (56)	593 (50)	10 (28)	−45 (22)	87 (56)
C_2A	−0.0208 (3)	0.2421 (7)	−0.0036 (7)	212 (16)	961 (87)	791 (58)	−42 (31)	−123 (27)	84 (56)
C_3	0.0974 (3)	0.2098 (7)	−0.0157 (6)	228 (16)	834 (72)	472 (48)	−6 (31)	−44 (23)	−80 (55)
C_4	0.1395 (3)	0.3172 (6)	0.0068 (7)	235 (18)	623 (62)	870 (68)	21 (30)	109 (31)	170 (53)
N_5	0.1575 (2)	0.3350 (5)	0.1142 (5)	205 (13)	570 (51)	76 (51)	−28 (21)	26 (22)	7 (44)
C_6	0.2019 (4)	0.4316 (7)	0.1402 (7)	321 (23)	568 (65)	1032 (78)	−155 (32)	88 (36)	−50 (61)
C_7	0.2668 (3)	0.3814 (8)	0.1644 (8)	208 (18)	1163 (91)	1134 (83)	−242 (34)	74 (33)	−177 (78)
C_8	0.2683 (3)	0.2585 (8)	0.2220 (7)	174 (15)	1406 (110)	1032 (77)	−40 (31)	39 (27)	−224 (72)
N_9	0.2160 (2)	0.2421 (5)	0.3063 (5)	145 (11)	856 (65)	794 (49)	−10 (21)	−4 (19)	−134 (45)
C_{10}	0.2238 (3)	0.2495 (7)	0.4174 (7)	179 (15)	1041 (96)	821 (63)	−23 (28)	−145 (25)	−111 (59)
C_{11}	0.1690 (3)	0.2435 (7)	0.4984 (6)	206 (16)	840 (77)	645 (52)	24 (29)	−110 (25)	−176 (50)
C_{12}	0.1237 (3)	0.3442 (7)	0.4670 (6)	213 (17)	806 (73)	732 (60)	−6 (29)	−69 (28)	−288 (56)
C_{12}A	0.1001 (5)	0.4231 (8)	0.5686 (7)	404 (27)	115 (96)	725 (69)	61 (43)	−4 (37)	−490 (71)
N_{13}	0.1076 (2)	0.3481 (5)	0.3554 (4)	163 (12)	695 (55)	563 (45)	18 (21)	−58 (20)	−70 (42)
C_{14}	0.0619 (4)	0.4372 (7)	0.3135 (7)	264 (19)	712 (69)	858 (68)	126 (31)	−14 (32)	−126 (60)
C_{15}	−0.0019 (3)	0.3803 (8)	0.3037 (7)	207 (17)	986 (82)	981 (72)	170 (31)	−21 (31)	−119 (70)
C_{16}	−0.0017 (3)	0.2471 (6)	0.2636 (6)	166 (13)	930 (85)	664 (53)	−12 (23)	2 (22)	11 (53)
N_{17}	0.1504 (2)	0.0928 (5)	0.1297 (5)	172 (13)	679 (53)	632 (47)	26 (20)	14 (20)	−79 (42)
C_{18}	0.1304 (3)	0.0953 (6)	0.0215 (6)	191 (15)	711 (64)	542 (51)	−44 (29)	46 (26)	−54 (46)
C_{18}A	0.1355 (4)	−0.0051 (7)	−0.0667 (7)	36 (24)	923 (79)	654 (60)	14 (40)	41 (35)	−234 (56)
N_{19}	0.1186 (2)	0.1051 (5)	0.3699 (5)	188 (13)	619 (52)	548 (44)	−35 (20)	−28 (20)	−15 (39)
C_{20}	0.1378 (3)	0.1207 (7)	0.4755 (6)	184 (15)	868 (68)	555 (53)	106 (31)	−29 (26)	−12 (49)
C_{20}A	0.1344 (4)	0.0298 (8)	0.5746 (7)	327 (23)	126 (98)	682 (62)	−88 (43)	−62 (36)	249 (65)

Atom	x	y	z	B, Å^2	Atom	x	y	z A	B, Å^2
H_3	0.090	0.200	−0.105	5.0	H_{14}B	0.075	0.465	0.235	4.0
H_4	0.160	0.370	−0.055	5.0	H_{15}A	−0.020	0.360	0.390	5.0
H_6A	0.210	0.500	0.080	6.0	H_{15}B	−0.020	0.420	0.230	5.0
H_6B	0.190	0.480	0.215	6.0	H_{16}A	0.010	0.190	0.330	5.0
H_7A	0.300	0.400	0.100	6.0	H_{16}B	−0.040	0.210	0.250	5.0
H_7B	0.290	0.440	0.220	6.0	H_{17}	0.175	0.020	0.165	4.0
H_{10}	0.265	0.260	0.450	5.0	H_{18}A	0.265	0.200	0.150	4.0
H_{11}	0.185	0.245	0.585	5.0	H_{18}B	0310	0.240	0.260	6.0
H_{14}A	0.055	0.500	0.380	5.0	H_{19}	0.095	0.030	0.340	4.0

[a] The form of the anisotropic temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The isotropic temperature factors are in Å. Standard errors are given in parentheses. If no standard error, the parameter was not refined.

as standards (062; 119; 15,0,3) and measured every 100 reflections, showed an apparently systematic drift of ±2% with time for which no correction was made. A total of 3492 reflections were collected with $(\sin\theta)/\lambda$ less than 0.65, 2795 of which had $I > 2\sigma(I)$.

The data were corrected for background following which Lorentz and polarization factors were applied to obtain the structure factors. Standard deviations were calculated according to the equation

$$\sigma^2(I) = 10C + 9 + g^2(10B + 18)$$

where C is the scan count, B the total background count, and g is the ratio of the time spent in scanning to that in measuring background. The net integrated intensity is given by $I = C - gB$. The numerical constants allow for truncation of the scalar digit by the diffractometer. The standard deviation on the structure factor was $\sigma(F^2)/2F$. The linear absorption coefficient was calculated as 8.12 cm^{-1} and an absorption correction was applied using the Gaussian interval method of Busing and Levy.[14] Corrections of F^2 ranged from 1.17 to 1.27. Wilson's method was then used to bring the F^2 to a relatively absolute value.

The structure was solved by superposition methods during which the positions of most of the atoms were located.[14] Neutral scattering factors for Fe, P, F, C, and N were obtained from Hanson, Herman, Lea, and Skillman,[15] and for H from Stewart et al.[16] Anomalous scattering factor tables for Fe and P were those of Cromer and Liberman.[17] Five cycles of least-squares refinement, during which the atom positions and overall temperature factors were varied, resulted in $R_1 = 0.29$ and $R_2 = 0.36$ where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.[18] Examination of the difference Fourier at this stage revealed not the expected linearly coordinated acetonitriles but peaks which indicated the presence of two bent acetonitriles in the cis configuration. Also one of the PF_6 anions was found to be partially disordered about a fourfold axis extending through two trans fluorines. The four fluorines were assigned occupancy factors of 0.75 and the four generated by a $\pi/4$ rotation about the axis, 0.25. Subsequent refinement of the occupancies showed these assignments to be essentially correct. Three cycles of refinement resulted in isotropic convergence at $R_1 = 0.105$ and $R_2 = 0.136$.

In order to test whether the proposed model represented the correct absolute configuration of the molecule, the signs of $\Delta f''$ in the anomalous scattering factor tables of the iron and phosphorus were changed. Three cycles of rerefinement resulted in $R_2 = 0.141$. By applying Hamilton's R test[19] to R_2 it was ascertained that the difference in R values was significant to the 5% level of probability. Hence the original structure was shown to be correct in chirality.

The subsequent difference Fourier showed the presence of regions of relatively high electron density (~0.7 e/Å) which could be attributed to hydrogen atoms. The C–H and N–H distances were adjusted to ~1.0 Å. The three final cycles of refinement in which the temperature factors of all of the atoms except the hydrogens were varied anisotropically and all of the hydrogens except for methyl hydrogens were included as fixed atoms resulted in convergence at $R_1 = 0.065$ and $R_2 = 0.080$. The final difference Fourier showed the presence of no peaks above 0.5 e/Å. Final positional and thermal parameters and structure factor tables are given in Table III.

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Registry No. $[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$, 56689-50-0.

Supplementary Material Available: A listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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An Electron Diffraction Investigation of the Molecular Structure of Monochlorodiborane, B_2H_5Cl

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The molecular structure of chlorodiborane, B_2H_5Cl, has been investigated at room temperature by gaseous electron diffraction. The results are consistent with a molecule of C_s symmetry having, except for the chlorine atom, the symmetry of diborane itself. Because the B–B and B–Cl distances are very similar, it was possible to measure accurately only their average value. However, an assumption based on results from other molecules allowed the deduction of reasonably accurate values for each. The more important distances (r_a), bond angles, and root-mean-square amplitudes of vibration (l) have the following values with parenthesized uncertainties estimated at 2σ: $r(\text{B–Cl,B})_{\text{av}} = 1.775$ (2) Å, $r(\text{B–Cl}) = 1.775$ (5) Å, $r(\text{B–B}) = 1.775$ (15) Å, $r(\text{B–H})_{\text{av}} = 1.277$ (2) Å, $r(\text{B–H}_t) = 1.205$ (13) Å, $r(\text{B–H}_b) = 1.331$ (15) Å, $\angle\text{BBCl} = 120.9$ (3)°, $\angle\text{H}_t\text{BH}_t = 125.0$ (60)°, $l(\text{B–Cl}) = 0.057$ (3) Å, $l(\text{B–B}) = 0.060$ (3) Å, $l(\text{B–H}_t) = 0.090$ (13) Å, $l(\text{B–H}_b) = 0.107$ (13) Å, and $l(\text{B}\cdots\text{Cl}) = 0.084$ (5) Å. Amplitudes of vibration calculated from an approximate force field fitted to the frequency spectrum are in good agreement with observed values.

It is well-known that the boron hydrides have unusual structures characterized by two different types of bonds between boron and hydrogen atoms, commonly called "bridge" and "terminal" bonds. Simple derivatives of the boron hydrides may be obtained by substitution at either bridge or terminal positions, but bridge substitution is perhaps less common and appears to perturb the structure of the rest of the molecule rather more than the other type. Thus, in the bridge-substituted compounds amino-[1,2] and dimethylaminodiborane[2] the B–B distance is about 0.14 Å longer than in diborane[3-5] itself, whereas in the terminal-substituted compounds monobromo-[6] and *cis*- and *trans*-1,2-dimethyl-[7] and 1,1,2,2-tetramethyldiborane[8] the increase in this distance is less than half this amount.

The differences between the structures of the boron hydride molecules and their derivatives remain an interesting and incompletely understood matter. We report here the results of an electron diffraction investigation of monochlorodiborane, another molecule with the substituent at the terminal position (Figure 1). During the course of the analysis we had occasion to calculate amplitudes of vibration from an approximate vibrational force field for the molecule; those results are also presented.

Experimental Section

The sample of essentially pure B_2H_5Cl was prepared for us by Professor David M. Ritter and kept at liquid nitrogen temperature until use.

The diffraction experiments were made in the OSU apparatus with the nozzle tip at room temperature. Other experimental conditions were an r^3 sector, 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1, 0.3–0.4-μA beam currents, 45–150-s exposure times, 0.056 90–0.056 96-Å