

Measurements of Structural and Quadrupolar Coupling Parameters for Chloroferrocene Using Microwave Spectroscopy

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Rotational spectra for two isotopomers of chloroferrocene were measured using pulsed-beam Fourier transform microwave spectroscopy. Transitions were observed for ³⁵Cl and ³⁷Cl isotopomers in the 4–10 GHz range. Chlorine quadrupole coupling strengths and rotational constants were obtained from the data. The rotational constants and quadrupole coupling strengths for ³⁵Cl are $A = 1370.009(8)$ MHz, $B = 767.342(1)$ MHz, $C = 634.8834(6)$ MHz, $eQq_{aa} = -9.06(4)$ MHz, and $eQq_{bb} = -28.43(6)$ MHz and for ³⁷Cl are $A = 1362.23(2)$ MHz, $B = 751.623(2)$ MHz, $C = 622.324(1)$ MHz, $eQq_{aa} = -8.78(18)$ MHz, and $eQq_{bb} = -20.76(9)$ MHz. These measured rotational constants were used to determine the following structural parameters of chloroferrocene: $r(\text{Fe}-(\text{C}_5\text{H}_5)) = 1.594(20)$ Å, $r(\text{Fe}-(\text{C}_5\text{H}_4\text{Cl})) = 1.699(13)$ Å, $r(\text{C}-\text{Cl}) = 1.7204(9)$ Å, and $r(\text{C}-\text{C}) = 1.4329(7)$ Å. No evidence for internal rotation was observed in the microwave spectrum.

Introduction

The structure of ferrocene and its derivatives has been of considerable interest since the compound was first characterized.¹ The solid state structures of ferrocene and of many ferrocene derivatives were determined using X-ray crystallography.^{2,3} In some cases there were considerable difficulties in obtaining structural information due to disorder in the crystal and internal motion of the Cp (cyclopentadienyl) groups.^{2,3} The lack of a dipole moment in ferrocene precludes any rotational spectroscopy study of the structure for unsubstituted ferrocene in the gas phase, but the singly substituted derivative chloroferrocene can be readily studied. The structure of solid dichloroferrocene has been previously studied⁴ but a previous structural study of chloroferrocene has not been reported. Chloroferrocene has been studied with infrared spectroscopy,⁵ iron-57 and carbon-13 NMR spectroscopy,⁶ Mossbauer spectroscopy,⁷ photoelectron spectroscopy (PES),⁸ and mass spectrometry.⁹

The only other information about the gas phase structures of substituted ferrocenes comes from the infrared and PES studies. Several vibrational transitions of substituted ferrocenes were found in an infrared study,⁵ but no torsional vibration is listed for any of the compounds. This could indicate the possibility of hindered internal rotation. The PES studies of chlorinated ferrocenes provide the only data for the gas phase compound. The spectrum obtained indicates that the chlorine substitution

on the Cp ring reduces the local symmetry of the π orbitals from D_{5h} to C_{2h} . This removes the degeneracy of the two e symmetry orbitals, and they become a and b symmetry orbitals. For the lower energy gerade orbitals, the splitting in chloroferrocene is 1.34 eV. The a_g and b_g orbitals of CpCl are both filled and are in a bonding arrangement with the d orbitals of the iron. This restricts the CpCl orientation with respect to the iron d orbitals. However, the other unsubstituted Cp group retains local D_{5h} symmetry and has no bonding orientation restrictions.

The variation in Fe–Cp bond length in the solid state with substitution has been observed in previous work and can be rationalized by considering the electronegativities of the Cp substituents. For Me_5Cp , the Fe–Cp bond length is shortened because methyl groups are less electron withdrawing than protons. Conversely, persubstitution by chlorine should lengthen the Fe–Cp bond length because the chlorine atoms remove electron density from the bonding orbitals in the π ring. Therefore, single substitution by chlorine would be expected to increase the Fe–Cp bond distance for bonds involving the Cl-substituted ferrocene. However, no significant lengthening of this bond was observed in the X-ray structure of dichloroferrocene.

Experimental Section

The sample was synthesized from ferrocene through the intermediate ferrocenylboric acid following the techniques published by Epton¹⁰ and Perevalova.¹¹ The sample was sublimed at just below its melting point for further purification and determination of the volatility. Characterization of the compound was performed on a Nicolet FTIR instrument in a gas cell; infrared transitions characteristic of chloroferrocene were observed at 3106.5 (s), 1414.5 (m), 1383.3 (w), 1359.4 (w), 1346.9 (w), 1207.2 (vw), 1177.0 (vw), 1166.6 (m), 1105.8 (m), 1052.8 (vw), 1019.5 (m), 1000.7 (m), 882.0 (m), 820.3 (m) and 811.7 (m) cm^{-1} . These observed transitions agree well with infrared data presented by Phillips, Lacey, and Cooper.⁵ The microwave spectrum was scanned in the 4–10 GHz range using a Flygare–Balle type spectrometer system.¹² The sample and pulse valve (General Valve 9-181) were maintained at 45–55 °C to produce sufficient vapor pressure of the

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Table 1. Measured Transition Frequencies (MHz), Relative Intensities (Int) and Quantum Numbers for ^{35}Cl -Ferrocene Rotational Transitions

measd	calcd	diff	int	J'	K'	$2F'$	J	K	$2F$
4132.1238(13)	4132.117	+0.007	20	3	0	9	2	0	7
5309.5827(20)	5309.583	+0.001	20	4	-1	9	3	-1	7
5310.4115(20)	5310.412	+0.002	20	4	-1	11	3	-1	9
5433.4624(24)	5433.462	+0.001	25	4	0	9	3	0	7
5433.5701(53)	5433.570	0.000	15	4	0	7	3	0	5
5435.7688(15)	5435.767	+0.002	25	4	0	11	3	0	9
5435.8720(41)	5435.884	-0.012	15	4	0	5	3	0	3
6474.6984(10)	6474.694	+0.004	28	5	0	7	4	-1	5
6475.5849(26)	6475.594	-0.010	23	5	0	9	4	-1	7
6475.7142(8)	6475.713	+0.001	23	5	0	13	4	-1	11
6476.6231(5)	6476.618	+0.005	25	5	0	11	4	-1	9
6610.4943(12)	6610.497	-0.003	35	5	-1	9	4	-1	7
6611.0573(25)	6611.058	-0.001	25	5	-1	11	4	-1	9
6611.2609(15)	6611.267	-0.006	25	5	-1	7	4	-1	5
6611.8120(9)	6611.809	+0.003	35	5	-1	13	4	-1	11
6704.8996(10)	6704.903	-0.004	30	5	0	9	4	0	7
6706.9102(9)	6706.909	+0.001	80	5	0	13	4	0	11
6839.3580(17)	6839.351	+0.007	30	5	-1	11	4	0	9
6843.0071(13)	6843.005	+0.002	36	5	-1	13	4	0	11
6967.1904(23)	6967.191	0.000	46	5	2	11	4	2	9
6967.3935(21)	6967.395	-0.001	21	5	2	9	4	2	7
7053.5992(14)	7053.602	-0.003	10	5	4	11	4	-4	9
7054.8317(68)	7054.835	-0.004	20	5	4	13	4	-1	11
7055.9270(35)	7055.928	-0.001	20	5	-4	13	4	4	11
7060.8752(13)	7060.865	+0.010	20	5	-3	11	4	3	9
7061.1861(22)	7061.180	+0.006	24	5	3	9	4	3	7
7061.5362(43)	7061.540	-0.004	28	5	-3	13	4	3	11
7061.8570(41)	7061.854	+0.003	10	5	3	7	4	-3	5
7097.8129(14)	7097.812	+0.001	30	5	3	13	4	-3	11
7097.9533(51)	7097.955	-0.002	30	5	-3	7	4	3	5
7236.0066(15)	7236.013	-0.007	18	5	1	11	4	1	9
7827.7669(46)	7827.768	-0.002	15	6	0	9	5	-1	7
7827.938(10)	7827.937	+0.002	20	6	0	11	5	-1	9
7828.3577(79)	7828.362	0.000	20	6	0	15	5	-1	13
7828.523(15)	7828.516	+0.007	25	6	0	13	5	-1	11
7901.7355(27)	7901.736	0.000	50	6	-1	11	5	-1	9
7902.1140(28)	7902.114	0.000	70	6	-1	13	5	-1	11
7902.4262(14)	7902.429	-0.003	60	6	-1	9	5	-1	7
7902.8149(61)	7902.817	-0.002	70	6	-1	15	5	-1	13
7962.8366(38)	7962.839	-0.003	22	6	0	11	5	0	9
9147.0809(47)	9147.078	+0.003	3	7	0	17	6	-1	15
9184.8262(35)	9184.827	-0.001	10	7	-1	13	6	-1	11
9185.1118(30)	9185.114	-0.002	10	7	-1	15	6	-1	13
9185.4451(23)	9185.450	-0.005	5	7	-1	11	6	-1	9
9185.7383(72)	9185.740	-0.001	10	7	-1	17	6	-1	15
9220.2996(59)	9220.295	+0.004	10	7	0	13	6	0	11
9220.4647(84)	9220.464	+0.001	10	7	0	15	6	0	13
9221.5343(43)	9221.533	+0.002	10	7	0	17	6	0	15
9260.1046(59)	9260.111	-0.007	3	7	-1	11	6	0	9
9260.2007(53)	9260.195	+0.006	3	7	-1	17	6	0	15
10481.4361(69)	10481.437	-0.001	3	8	0	15	7	0	13
10481.6166(23)	10481.617	0.000	3	8	0	17	7	0	15
10482.1985(47)	10482.203	-0.004	3	8	0	13	7	0	11
10482.3892(52)	10482.384	+0.005	3	8	0	19	7	0	17

sample. The sample, mixed with neon at 0.6–1.0 atm, was pulsed into a Fabry–Perot microwave cavity for observation of the spectra. The microwave pulse length is typically 0.1 μs , and the observed line widths (fwhm) are about 20 kHz with the neon carrier gas. The statistical uncertainty in line center measurements ranges from 0.5 to 8 kHz, depending on the line strength and residual broadening due to unresolved components. This statistical uncertainty (1σ) is given, in parentheses, for each transition in Tables 1 and 2. Systematic errors are much smaller than this since frequency calibrations are made with respect to WWVH. Reasonably strong transitions with typical quadrupole splitting patterns were observed for $J' \leftarrow J = 3 \leftarrow 2$ through $8 \leftarrow 7$. The measured transitions are listed in Tables 1 and 2. The “int” column lists approximate, relative intensities. The “ K ” values are values for K_p , with minus signs indicating the lower energy K value, and $K_p = |K|$. The value for K_o is obtained from $K_o = J - K_p + (K_p - K)/2K_p$.

Table 2. Measured Transition Frequencies (MHz), Relative Intensities (int), and Quantum Numbers for ^{37}Cl -Ferrocene Transitions

measd	calcd	diff	int	J'	K'	$2F'$	J	K	$2F$
4051.0559(21)	4051.058	-0.002	1	3	0	3	2	0	1
5329.3348(32)	5329.344	-0.010	10	4	0	9	3	0	7
5331.0628(33)	5331.071	-0.009	8	4	0	11	3	0	9
6480.6339(12)	6480.637	-0.003	20	5	-1	9	4	-1	7
6481.0839(21)	6481.087	-0.003	30	5	-1	11	4	-1	9
6481.2293(49)	6481.236	-0.006	20	5	-1	7	4	-1	5
6481.6716(7)	6481.672	-0.001	30	5	-1	13	4	-1	11
6577.2304(12)	6577.237	-0.007	18	5	0	9	4	0	7
6577.2746(18)	6577.267	+0.007	20	5	0	11	4	0	9
6578.7589(12)	6578.760	-0.001	25	5	0	7	4	0	5
6578.7860(7)	6578.788	-0.002	13	5	0	13	4	0	11
6720.6478(11)	6720.647	0.000	18	5	-1	11	4	0	9
6720.9874(28)	6720.984	+0.003	10	5	-1	9	4	0	7
6723.4833(24)	6723.482	+0.001	5	5	-1	13	4	0	11
6723.8351(15)	6723.833	+0.002	1	5	-1	7	4	0	5
7094.6459(16)	7094.643	+0.003	20	5	1	13	4	1	11
7666.9366(81)	7666.937	0.000	12	6	0	9	5	-1	7
7667.1074(73)	7667.102	+0.006	10	6	0	11	5	-1	9
7667.4170(90)	7667.416	+0.001	11	6	0	15	5	-1	13
7667.5746(61)	7667.569	+0.005	10	6	0	13	5	-1	11
7747.0832(24)	7747.081	+0.002	15	6	-1	11	5	-1	9
7747.3928(48)	7747.386	+0.007	32	6	-1	13	5	-1	11
7747.6143(38)	7747.615	-0.001	20	6	-1	9	5	-1	7
7747.9326(78)	7747.928	+0.005	20	6	-1	15	5	-1	13
7810.8589(16)	7810.849	+0.010	25	6	0	11	5	0	9
7810.9474(45)	7810.949	-0.002	20	6	0	13	5	0	11
7812.0094(60)	7812.010	0.000	40	6	0	9	5	0	7
7812.1208(19)	7812.110	+0.011	25	6	0	15	5	0	13
9005.4939(33)	9005.500	-0.006	1	7	-1	13	6	-1	11
9006.2051(10)	9006.212	-0.007	1	7	-1	17	6	-1	15
9043.2312(47)	9043.231	0.000	5	7	0	13	6	0	11
9043.3653(36)	9043.368	-0.002	5	7	0	15	6	0	13
9044.0590(63)	9044.064	-0.005	6	7	0	11	6	0	9
9044.1989(63)	9044.201	-0.002	6	7	0	17	6	0	15

Table 3. Molecules Constants Obtained from Data Analysis^a

constant	^{35}Cl -ferrocene	^{37}Cl -ferrocene
A , MHz	1370.0094(76)	1362.230(24)
B , MHz	767.3424(11)	751.6231(18)
C , MHz	634.8834(6)	622.3241(12)
eQq_{aa} , MHz	-9.06(4)	-8.78(18)
eQq_{bb} , MHz	-28.43(6)	-20.76(9)
D_J , kHz	0.28(5)	-0.41(18)
D_{JK} , kHz	-0.23(27)	-4.6(4)
σ_{fit} , kHz	4.5	5.6

^a The 88 measured lines listed in Tables 1 and 2 were included in the least-squares fits to determine the molecular parameters, 54 for ^{35}Cl -ferrocene and 34 for ^{37}Cl -ferrocene. Using a seven-parameter asymmetric rigid rotor, with quadrupole, model gives the molecular constants above. The final values are listed with 2σ error limits.

Data Analysis

The observed transitions were fit using seven adjustable parameters in the Hamiltonian for each isotopomer. The adjustable parameters were the rotational and distortion constants A , B , C , D_J , and D_{JK} and the eQq_{aa} , and eQq_{bb} quadrupole coupling strengths. A total of 88 lines were included in the fits, 54 for ^{35}Cl - and 34 for ^{37}Cl -ferrocene. Standard deviations for fits to the measured transitions are less than 6 kHz. The values of the parameters obtained are listed in Table 3. Nineteen measured lines were not included, and these may be due to the less abundant isotopomers containing iron-54 or carbon-13. The distortion constants are smaller than the statistical errors on these parameters but were included. A five-parameter fit (without these distortion constants) for each isotope produced fits with standard deviations of less than 20 kHz, but the small distortion effects had effectively been absorbed into the quadrupole terms. This produced larger errors in these quadrupole terms, and an unacceptable ratio of eQq_{cc} values for the chlorine isotopes of ~ 1.25 . The ratio of chlorine quadrupole coupling strengths for the two isotopes has been previously

Table 4. Quadrupole Coupling Components for the C–Cl Bond Axis System^a

constant	value
$eQq_{zz} (^{35}\text{Cl})$	–63.3 MHz
$eQq_{xx} (^{35}\text{Cl})$	25.8 MHz
$eQq_{yy} (^{35}\text{Cl}) = eQq_{cc} (^{35}\text{Cl})$	37.49(9) MHz
$\eta = (eQq_{xx} (^{35}\text{Cl}) - eQq_{yy} (^{35}\text{Cl}))/eQq_{zz} (^{35}\text{Cl})$	0.18
$eQq_{zz} (^{37}\text{Cl})$	–47.8 MHz
$eQq_{xx} (^{37}\text{Cl})$	18.2 MHz
$eQq_{yy} (^{37}\text{Cl}) = eQq_{cc} (^{37}\text{Cl})$	29.55(31) MHz
$\eta = (eQq_{xx} (^{37}\text{Cl}) - eQq_{yy} (^{37}\text{Cl}))/eQq_{zz} (^{37}\text{Cl})$	0.24

^aThe *x* axis is perpendicular to both the ring and the bond, *y* is the axis perpendicular to the bond and in the plane of the carbon ring, and *z* is along the bond axis.

reported to very high accuracy.¹³ In this molecule, the ratio can only be computed directly from the quadrupole terms along the *c* axis of the molecule since this axis is common to both isotopomers. For each isotope, this component can be obtained using the relation

$$eQq_{cc} = -(eQq_{aa} + eQq_{bb})$$

since the quadrupole tensor is traceless. Using the values of eQq_{aa} and eQq_{bb} from the line fits, the ratio is determined to be

$$eQq_{cc} (^{35}\text{Cl})/eQq_{cc} (^{37}\text{Cl}) = 1.268(38)$$

in close agreement with the previous value.¹³ The inclusion of the distortion parameters improved this ratio and the agreement of other parameters. The quadrupole coupling values obtained in the fit are projected along the principal axes of the moments of inertia. Rotation of these axes into a more suitable molecular frame allows comparison of the electric field gradients around the C–Cl bond. Axes were chosen for this analysis with the *z* axis in the direction of the C–Cl bond and the *x* axis perpendicular to the C–Cl bond direction and passing through the center of mass. The principal-axis quadrupole coupling tensor was transformed into this framework using standard matrix methods. The rotation angle Θ , between the *a* and *z* axes, was determined from the structural data. For ³⁵Cl–ferrocene, $\Theta = 51.27(4)^\circ$, with a slightly smaller value, $50.23(4)^\circ$, for ³⁷Cl–ferrocene. The quadrupole coupling strengths in this bond axis system are given in Table 4. The field gradient asymmetry parameter η can be obtained from these values. For ³⁵Cl–ferrocene, $\eta = 0.18$, and for ³⁷Cl–ferrocene, $\eta = 0.24$. The difference in these η values is probably due to a small misalignment between the C–Cl bond direction and the principal axis system of the quadrupole coupling tensor. With only a 1° difference between the principal axis systems for the two isotopomers, no meaningful value for this misalignment can be obtained.

Since an excellent fit was obtained using a rigid-rotor model, relatively small values for distortion constants were obtained, and patterns of transitions characteristic of internal rotation were not observed, we believe that this molecule has a relatively high barrier to internal rotation.

The four-parameter least-squares fit to obtain the structural parameters was done with three restrictions: the carbon rings are assumed to be coplanar, *C*₅ symmetry was assumed for the Cp groups, and the C–H bond length was fixed at 1.08 Å. Previous structural work for solid state ferrocenes has indicated that the hydrogen atoms are slightly bent out of the carbon plane toward the Fe atom. Restricting the hydrogen atoms to the plane of the Cp carbon atoms would not be expected to introduce very large error in the fit, since the H atoms have a small mass and the displacements from the Cp plane would cause quite small changes in the moments of inertia. In order to test these effects, however, other fits were carried out with the H atoms displaced from the Cp carbon plane. When the hydrogen atoms on each ring were bent out of the carbon plane, it was found that this structural change was weakly correlated with the two iron to Cp ring distances. The angle was then fixed at 4.6° , the value reported for

Table 5. Skeletal Structural Parameter^a

bond	value, Å	bond	value, Å
Fe–(C ₅ H ₅)	1.594(20) ^b	C–Cl	1.7204(9)
Fe–(C ₅ H ₄ Cl)	1.699(13) ^b	C–C	1.4329(7)

^aThe six rotational constants for the two isotopomers were used in a nonlinear least squares fit to determine the four key structural parameters given above. Five-fold symmetry of the carbon rings was assumed, the two Cp rings were required to be coplanar, the C–H bond length was fixed at 1.08 Å with a carbon plane–carbon–hydrogen angle of 4.6° from the electron diffraction study. Final values are listed with 2σ error limits. ^bThese error limits are propagated from the standard deviation given for the carbon plane–carbon–hydrogen angle ($4.6 \pm 2.7^\circ$).¹⁴ Due to correlation of these parameters and this angle, the quoted errors are larger than 2σ from the fit by a factor of 3. The 2σ errors for these two parameters are 0.006 and 0.004 Å.

ferrocene by Bohn and Haaland.¹⁴ This is believed to be the best value for several reasons; the microwave data are in relatively good agreement with the gas phase electron diffraction data, and the standard deviations of all the fits done at different angles were at a minimum between 4 and 6° . Furthermore, the errors propagated from the error in the angle from the electron diffraction work are more likely to represent the true error in the correlated parameters. The four structural parameters chosen to be the variable parameters for the fit are the Fe–(C₅H₅) and Fe–(C₅H₄Cl) distances and the C–Cl and C–C bond lengths. The Fe–(C₅H₅) distance is the perpendicular distance of the iron from the center of the carbon ring. These parameters define the “skeleton” of the chloroferrocene molecule. The final values for the structural parameters are listed in Table 5.

Conclusions

This is the first structural study of chloroferrocene and the first structural study of a substituted ferrocene in the gas phase. The lack of observable internal rotation for the ferrocene frame was a pleasant surprise, since it made the assignment of the spectrum relatively straightforward. The structural fit provided accurate values for all of the bond lengths, even though only two isotopomers were analyzed. The electronic structure information found for the C–Cl bond indicates significant deviation from cylindrical symmetry, apparently due to an anisotropic distribution of π electrons for the directions in the plane and perpendicular to the plane of the carbon ring. The anisotropy parameter η is a direct indication of this effect. Since the values of η for the two isotopomers are slightly different, it appears that the principal axis of the quadrupole coupling tensor is not exactly aligned with the C–Cl bond. The present experimental value of $eQq_{zz} (^{35}\text{Cl}) = -63.3$ MHz is significantly smaller than the value of $eQq_{zz} (^{35}\text{Cl}) = -71.1$ MHz measured for chlorobenzene.¹⁵ This could be due to a decrease in the unbalance of p-electron density on chlorine as the CpCl ligand gains negative charge upon formation of the complex.

The results support the trend of increasing Fe–Cp bond length upon electronegative substitution of the carbon ring. In this particular case, the substitution of a single chlorine atom appears to increase the Fe–Cp bond length by 0.11(3) Å. The Fe–Cp bond length, 1.594(20) Å, was found to be significantly shorter than the solid state value of 1.654 Å for ferrocene. The difference in the gas phase and solid state values is more likely due to interactions in the crystal than the effects of the chlorine substitution of the other ring. In the solid state, the ferrocene molecules are packed into either a triclinic or a monoclinic crystal lattice,^{2,3} where the π systems of the Cp groups can interact through space in the crystal much like the π systems in graphite. Such an interaction would tend to decrease the strength of the Fe–Cp bond. In the gas phase, the molecules

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Table 6. Measured and "Best-Fit" Rotational Constants (MHz)^a

constant	measd	calcd	diff
$A(^{35}\text{Cl})$	1370.0094	1369.9929	0.0165
$A(^{37}\text{Cl})$	1362.2306	1362.2704	-0.0398
$B(^{35}\text{Cl})$	767.3424	767.4005	-0.0581
$B(^{37}\text{Cl})$	751.6232	751.5850	0.0382
$C(^{35}\text{Cl})$	634.8834	634.8413	0.0421
$C(^{37}\text{Cl})$	622.3241	622.3721	-0.0480

^aThe bond lengths given in Table 5 give calculated rotational constants in very good agreement with measured values. $\sigma_{\text{fit}} = 75$ kHz.

are sufficiently distant from each other such that no π - π interactions are expected and the rich electron density of the Cp group is focused in the bond to the d orbitals of iron. A similar effect is presumed to occur for the CpCl group in comparison to the solid state, but the present gas phase value determined using the structure fit indicates a Fe-CpCl bond length 0.01(3) Å shorter than the one reported for solid dichloroferrocene.⁴ Therefore, it is difficult to determine whether the phenomenon is due to intramolecular effects or whether the π - π interactions in the solid phase are reduced by the presence of the chlorine. The value of Fe-Cp distance

obtained in the electron diffraction study is in reasonably good agreement with the microwave data when the hydrogen atoms are bent out of the Cp plane, toward the iron atom. Without further study of deuterated compounds, the microwave data do not allow an accurate value for the displacement of the hydrogen atoms toward the iron atom. The present, gas phase values for Fe-Cp distances give an excellent fit to the measured set of six rotational constants (see Table 6) and are quite reasonable when compared with solid state values, which leads us to believe that they are accurate within the quoted error limits.

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