AIP | The Journal of Chemical Physics

The gas-phase structure of chloroferrocene from microwave spectra

Brian J. Drouin, Jennifer J. Dannemiller, and Stephen G. Kukolich

Citation: The Journal of Chemical Physics **112**, 747 (2000); doi: 10.1063/1.480708
View online: http://dx.doi.org/10.1063/1.480708
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/112/2?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Rotational spectra of rare isotopic species of fluoroiodomethane: Determination of the equilibrium structure from rotational spectroscopy and quantum-chemical calculations
J. Chem. Phys. **137**, 024310 (2012); 10.1063/1.4731284

Microwave spectrum of o-benzyne produced in a discharge nozzle
J. Chem. Phys. **119**, 4353 (2003); 10.1063/1.1593015

The conformational structures and dipole moments of ethyl sulfide in the gas phase
J. Chem. Phys. **115**, 3057 (2001); 10.1063/1.1385527

Microwave spectra and structure of an isoxazole–CO Van der Waals complex
J. Chem. Phys. **109**, 5383 (1998); 10.1063/1.477157

Measurements of structural and quadrupole coupling parameters for bromoferrocene using microwave spectroscopy
J. Chem. Phys. **107**, 6541 (1997); 10.1063/1.474897

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.59.222.12 On: Thu, 27 Nov 2014 12:17:20

JOURNAL OF CHEMICAL PHYSICS VOLUME 112, NUMBER 2 8 JANUARY 2000

The gas-phase structure of chloroferrocene from microwave spectra

Brian J. Drouin,[a] Jennifer J. Dannemiller, and Stephen G. Kukolich[b]
Department of Chemistry, University of Arizona, Tueson, Arizona 85721

(Received 31 August 1999; accepted 13 October 1999)

Rotational spectra for ten isotopomers of chloroferrocene were measured using pulsed-beam Fourier transform microwave spectroscopy. Rotational transitions due to both ''*a*'' and ''*b*'' dipole moments were measured in the 4–12 GHz range. Thirty rotational constants were determined from microwave data for the normal, ^{54}Fe, ^{57}Fe, ^{37}Cl, and six unique ^{13}C isotopomers, by fitting the microwave data using a rigid rotor Hamiltonian with centrifugal distortion and quadrupole coupling terms. The moments of inertia of the isotopomers were used in Kraitchman and in least-squares fitting analyses to determine gas-phase structural parameters. The unsubstituted cyclopentadienyl (C_5H_5) ligand was determined to have essentially fivefold local symmetry, while the chlorinated cyclopentadienyl ligand shows small, but significant distortions from the fivefold symmetry. The C–Cl bond is bent 2.7(6)° from the plane of carbon atoms. This substituted C_5H_4Cl ligand is tilted 1.4(5)° with respect to the unsubstituted C_5H_5 ligand. The carbon atoms of the two cyclopentadienyl ligands are eclipsed, similar to normal ferrocene. The average Fe–C distance is 2.042(9) Å. The estimated displacement of C–H bonds out of the planes of the carbon atoms is 4(2)° away from the metal atom. © *2000 American Institute of Physics.* [S0021-9606(00)01002-3]

I. INTRODUCTION

Ferrocene has played a central role in the development of organometallic chemistry, and the structures of ferrocene and various derivatives have long been of particular interest in inorganic chemistry. A detailed description of the molecular structure is often very useful in understanding chemical and electronic properties, particularly in larger molecules. No recent diffraction data were found for ferrocenes with a single halogen substitution. Attempts to structurally characterize chloroferrocene by x-ray diffraction techniques were hampered by a highly disordered crystal lattice.[1] It has been shown that microwave spectroscopy[2] could be used to probe the structure of this type of compound in the gas phase. Chloroferrocene has been studied with IR spectroscopy,[3] iron-57 and carbon-13 nuclear magnetic resonance (NMR) spectroscopy,[4] Mossbaüer spectroscopy,[5] photoelectron spectroscopy,[6] and mass spectrometry.[7] Presently, the microwave work provides the only insight into structural details of these compounds. The previous microwave work[2] described detailed results for quadrupole coupling parameters, but only a few structural parameters could be obtained, since data for just the two chlorine isotopomers were measured. This seriously limited the structural analysis, since many correlated structural parameters could not be reliably determined from this small data set.

In the present work, the microwave spectrum has been investigated further, using an improved spectrometer with a low-noise *C*-band microwave amplifier. The main isotopomer spectra, observed between 4 and 10 GHz, exhibited a signal-to-noise ratio of ∼100:1 This represented a factor of 100 improvement over the spectra previously recorded for this compound, and this allowed measurements of spectra for many more isotopomers.

II. EXPERIMENT

The synthesis of this compound followed the methods published by Epton[8] and Perevalova.[9] The starting compound was ferrocene, from which the intermediate ferrocenyl boric acid was prepared. This compound was then converted to chloroferrocene through treatment with $CuCl_2$. The compound is apparently quite stable, since the previously prepared sample was still usable in the present work after considerable time in storage.

The microwave spectrum was scanned in the 4–10 GHz range using a Flygare–Balle-type spectrometer system. The sample and the pulse valve were kept at 45–55 °C to produce sufficient vapor pressure of the 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, full width at half maximum (FWHM), are about 20 kHz with the neon carrier gas.

A low-noise *C*-band microwave amplifier (MITEQ AFS3-04000800-10) was placed on the ''front end'' of the microwave receiver ahead of the MITEQ wideband balanced mixer. Since this amplification step occurs prior to the mixing step, a significant improvement in the signal-to-noise ratio is obtained. In addition to the modified microwave receiver system, a larger bore pulse valve was also used in the system. The bore size of a regular Series 9 general valve is 1 mm. Using special poppets, the bore size was increased to 2 mm to allow a greater portion of gas into the cavity per pulse. Using these modifications, and holding the sample at 55 °C, main isotopomer signals with ∼100:1 signal-to-noise ratio were obtained.

---

[a] Present address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

[b] Electronic mail: kukolich@u.arizona.edu

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.59.222.12 On: Thu, 27 Nov 2014 12:17:20

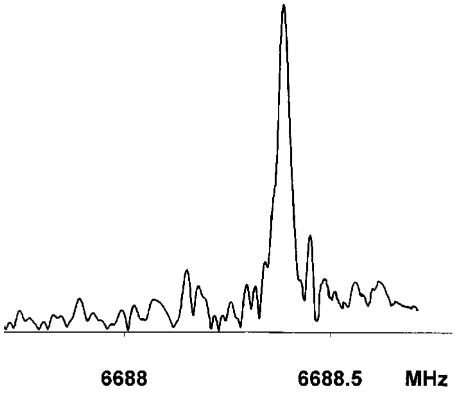

FIG. 1. Spectrum for the 5_{05}, $13/2 \leftarrow 4_{04}$, 11/2 transition at 6688.3864(33) MHz, for ^{13}C2 chloroferrocene. This spectrum was an average over 427 beam pulses.

The key to good microwave structural determination involves measurement of a large number of substituted isotopomer spectra. The previous data set only contained rotational constants for the two chlorine isotopomers of chloroferrocene. With the improved signal-to-noise ratios, spectra for ^{54}Fe(4%), ^{57}Fe(1%), and ^{13}C(2% and 1%) were readily measured. An example ^{13}C spectrum is given in Fig. 1 to illustrate a typical molecular signal.

III. DATA ANALYSIS

The new spectra for iron- and carbon-substituted isotopomers are given in Table I(a) and (b). The spectral data were analyzed using a least-squares fitting routine employing a rigid rotor Hamiltonian with centrifugal distortion and quadrupole coupling. Spectral parameters determined from the fitting analyses of the different isotopomer spectra are given in Table II. Data and spectral parameters for the most abundant and ^{37}Cl substituted isotopomer are given in Ref. 10. The Cartesian coordinates for all atoms are listed in Table III. These coordinates were obtained using the least-squares fit analysis, and were used for Fig. 2.

Each set of transitions contains up to four components, representing a quadrupole quartet (since only $\Delta F = \Delta J = +1$ transitions are included). Due to the abundance of available transitions (more than 60 were previously measured for ^{35}Cl-ferrocene without the amplifier!), only the strongest transitions were examined for the less-abundant isotopomers. The off-diagonal element eQq_{ab} slightly perturbs the quadrupole patterns. An accurate value for this term was obtained, following the study of bromoferrocene,[10] by comparing the properties of the respective halobenzenes.[10–12] Including this term significantly improves the spectral fits for the main isotopomers, particularly for the lower-J transitions with larger quadrupole splitting patterns. The off-diagonal quadrupole term is incorporated, and held constant, in the present least-squares fit analyses, which used Pickett's program SPFIT.[13] This term and other off-diagonal quadrupole terms are expected to change upon isotopic substitution due to the rotation of the inertial axis system. However, these off-diagonal terms are not expected to significantly change the rotational constants obtained for the subsequent structural analysis. Therefore, these parameters have been kept fixed at the values for the main isotopomer ($eQq_{ab} = 53.42$ MHz, $eQq_{ac} = eQq_{bc} = 0.0$ MHz).[10] Initial fits of the substituted isotopomers were done with fixed values for the diagonal components of the quadrupole tensor. The final fits presented in Table II were obtained by treating the values for eQq_{aa} and $eQq_{bb} - eQq_{cc}$ as adjustable parameters.

For accurate determination of the A, B, and C rotational constants, at least four sets of rotational transitions must be measured for each desired isotopomer. For verification of assignment of overlapping patterns of lines, a fifth set was measured and included in the analysis. Two of the rotational transitions are due to ''b''-type selection rules, and the remaining three are of ''a'' dipole type. Even though the molecule is quite asymmetric ($\kappa = 0.74$), measurement of a and b types of transitions helps to reduce uncertainties in the B and A rotational constants, respectively. The new spectra for iron- and carbon-substituted isotopomers are given in Table I(a) and (b). Data and spectral parameters for the main isotopomer and the ^{37}Cl-substituted isotopomer are given in Ref. 2.

IV. STRUCTURE DETERMINATION—LEAST-SQUARES FIT

The basic structure with numbering of the carbon atoms for chloroferrocene is shown in Fig. 2. Several different least-squares structural fits were performed in an effort to decide which parameters were best determined using the present data set, and to analyze correlation effects. A cylindrical coordinate system (see Fig. 3) is the preferred coordinate system for determining the structural parameters by fitting the measured rotational constants. The z axis was chosen to go through the iron atom (the origin) and the ''centers'' of the two cyclopentadienyl $[C_5H_4X(X=H,Cl)]$ ligands. The C_s symmetry plane is coincident with the xz and ab planes. The Cartesian coordinates x and y were determined from radial (r) and angular (θ) coordinates, in which θ is measured as an angle from the x axis in a plane perpendicular to the xz plane. Up to 19 parameters could be varied in a structure fit to all 30 rotational constants. The 19 parameters included seven z coordinates, one for the chlorine and each of the (nonequivalent) carbon atoms. Also included were: seven r coordinates, which included the chlorine and all (nonequivalent) carbon atoms, and four angular coordinates describing the angles between the radial carbon vectors, and one parameter describing the out of ''plane'' bend of the C–H bonds. The C–H bond lengths were fixed at 1.08 Å, and the bond directions were fixed to move along with the carbon atoms maintaining the radial symmetry within the cylindrical coordinate system (i.e., such that a line along the C–H bond would intersect the z axis). This fit gave very similar r and z values for all the carbon atoms of the unsubstituted C_5H_5 group, with angular values very close to those appropriate for fivefold symmetry. This is not surprising, due to the remote location of the chlorine ligand that perturbs the high symmetry of unsubstituted ferrocene. In order to reduce correlations between parameters, and to produce more precise values for the determined parameters, the positions for carbon atoms in the C_5H_5 group were all fit using only one z

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.59.222.12 On: Thu, 27 Nov 2014 12:17:20

TABLE I. (a). Measured transition frequencies for the ^{54}Fe, ^{57}Fe, and two ^{13}C isotopomers of chloroferrocene. The quantum numbers for the total angular momentum are: $G' = F' + 1/2$, and $G = F + 1/2$. Frequencies are given in MHz; experimental uncertainties (1σ) in parentheses. (b). Measured transition frequencies for ^{13}C isotopomers of chloroferrocene. Frequencies are given in MHz; experimental uncertainties (1σ) in parentheses.

(a)	$J'_{Kp',Ko'}$	G'	$J_{Kp,Ko}$	G	^{54}Fe	^{57}Fe	^{13}C(Cl)	^{13}C(C6)
	5_{05}	5	4_{04}	4	6709.2978(38)	6702.7536(31)		
	5_{05}	6	4_{04}	5	6709.3281(38)		6685.3582(27)	
	5_{05}	4	4_{04}	3			6687.3535(30)	
	5_{05}	7	4_{04}	6	6711.3133(11)	6704.7290(23)		6674.0308(67)
	6_{06}	5	5_{15}	4		7825.0434(45)	7802.1561(09)	
	6_{06}	6	5_{15}	5	7833.2722(5)	7825.2103(21)	7802.3475(32)	
	6_{06}	8	5_{15}	7	7833.4397(30)	7825.6351(49)		7796.4378(56)
	6_{06}	7	5_{15}	6	7833.8681(77)	7825.7911(47)		7796.5420(82)
	6_{16}	6	5_{15}	5	7834.0219(25)	7899.1020(36)		
	6_{16}	7	5_{15}	6	7907.0582(59)	7899.4811(28)		7864.7106(14)
	6_{16}	5	5_{15}	4	7907.4368(23)	7899.7929(22)	7878.4937(35)	7865.0262(39)
	6_{16}	8	5_{15}	7	7908.1413(12)	7900.1840(27)	7878.8945(25)	7865.4172(41)
	6_{16}	5	5_{15}	5	7919.6919(39)			7864.3257(24)
	6_{16}	6	5_{05}	5				7991.1693(44)
	6_{06}	6	5_{05}	5		7960.2449(38)		7922.8046(52)
	6_{06}	7	5_{05}	6	7968.1891(33)	7960.3587(34)	7939.7602(30)	
	6_{06}	5	5_{05}	4	7969.7009(21)	7961.7322(06)		
	6_{06}	8	5_{05}	7		7961.8647(39)		
	6_{16}	7	5_{05}	6	8041.6048(32)	8034.0478(63)	8015.0134(17)	
	6_{16}	6	5_{05}	5	8043.9733(36)	8034.1394(30)	8015.1116(35)	
	6_{16}	8	5_{05}	7		8036.4188(22)		7993.4090(47)
	6_{16}	5	5_{05}	4	8044.0387(35)			7993.4289(19)

(b)	$J'_{Kp',Ko'}$	G'	$J_{Kp,Ko}$	G	^{13}C(C2)	^{13}C(C3)	^{13}C(C7)	^{13}C(C8)
	5_{05}	5	4_{04}	4	6686.3180(23)	6672.0994(62)	6672.6316(18)	6657.3018(49)
	5_{05}	6	4_{04}	5		6672.1415(37)		
	5_{05}	4	4_{04}	3		6674.1189(76)		
	5_{05}	7	4_{04}	6	6688.3864(33)		6674.6373(16)	6659.2844(53)
	6_{06}	5	5_{15}	4	7807.3115(48)	7799.3417(46)		7765.1754(47)
	6_{06}	6	5_{15}	5	7807.4813(44)	7799.4188(51)	7790.8460(94)	7765.4022(15)
	6_{06}	8	5_{15}	7	7807.9089(51)	7799.9222(14)	7791.2533(35)	7765.7856(11)
	6_{06}	7	5_{15}	6	7796.1411	7799.9850(34)	7791.4221(61)	7766.0027(11)
	6_{16}	6	5_{15}	5	7880.7721(15)	7865.6179(39)	7864.2725(21)	7843.7546(45)
	6_{16}	7	5_{15}	6	7881.1509(11)	7865.9946(13)	7864.6476(08)	7844.1314(23)
	6_{16}	5	5_{15}	4	7881.4611(49)	7866.3173(20)	7864.9589(45)	7844.4299(50)
	6_{16}	8	5_{15}	7	7881.8559(18)	7866.7113(33)	7865.3530(36)	7844.8286(44)
	6_{16}	5	5_{15}	5		7989.1373(64)		
	6_{16}	6	5_{05}	5	7941.3904(15)			7906.7813(46)
	6_{06}	6	5_{05}	5	7941.4962(38)	7923.0582(20)	7925.0444	7906.8838(80)
	6_{06}	7	5_{05}	6	7942.8925(16)	7924.4086(10)	7926.4488(60)	
	6_{06}	5	5_{05}	4	7943.0144(16)	7924.5536(17)	7926.5701(33)	7908.4151(18)
	6_{06}	8	5_{05}	7	8014.5840(29)	7989.0813(22)	7998.2699(46)	7985.0234(51)
	6_{16}	7	5_{05}	6	8014.6809(19)		7998.3730(37)	7985.1403(59)
	6_{16}	6	5_{05}	5	8016.9640			7987.4604(07)
	6_{16}	8	5_{05}	7	8017.0306(70)			
	6_{16}	5	5_{05}	4				

and one r coordinate. Fixing the values of θ for C7, C10 and C8, C9 at 72° and 144°, respectively, gave this ligand local C_{5v} symmetry. This reduced the number of parameters in the fit to 13, and yielded more precise values for all varied parameters. Varied parameters did not change outside of the standard deviations given from the 19-parameter fit. The consistency between the fits provides confidence that the coordinates have been determined accurately.

The average value for the Fe–C bond lengths for the C_5H_5 ligand, of 2.048(5) Å, is slightly larger than the average Fe–C bond lengths for the C_5H_4Cl ligand, of 2.037(10) Å. We note that this difference is within the estimated errors for the parameters. These results represent an improvement over the previous report for these parameters,[2] which was determined using a much smaller data set. The new data reveal that the chlorine atom, not the entire C_5H_4Cl group, is moved further from the metal along the z axis. Furthermore, the previous assumption of a 4(2)° displacement of the C–H bond out of the carbon plane of the C_5H_5 (and C_5H_4Cl) group *towards* the metal is not supported by the present analysis. Although the present data do not include deuterated isotopomers, the data set still allows an approximate determination of this angle of 4(2)°, *away* from the metal.

The deviations of the coordinates for the carbon frame of the chlorinated cyclopentadienyl (C_5H_4Cl) group from the fivefold symmetry of an unsubstituted cyclopentadienyl

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.59.222.12 On: Thu, 27 Nov 2014 12:17:20

TABLE II. The spectral parameters for the low-abundance isotopomers of chloroferrocene, determined using least-squares fits. The carbon atom numbering is shown in Fig. 2. Values in MHz. The listed error limits are 1σ.

Parameter	^{54}Fe	^{57}Fe	^{13}C1	^{13}C2
A	1370.3086(42)	1369.8587(51)	1369.7742(52)	1362.0075(48)
B	767.8772(10)	767.0743(12)	764.6235(13)	764.5426(11)
C	635.3158(2)	634.6707(2)	632.9747(3)	633.3586(2)
eQq_{aa}	−8.754(14)	−9.169(43)	−9.248(56)	−9.006(13)
$eQq_{bb}-eQq_{cc}$	−65.81(2)	−65.77(22)	−66.149(38)	−65.993(19)
Parameter	^{13}C3	^{13}C6	^{13}C7	^{13}C8
A	1353.6448(42)	1358.5356(72)	1360.5853(49)	1368.1432(48)
B	766.7093(10)	766.1513(18)	763.0594(12)	760.1657(11)
C	631.6914(2)	631.5886(4)	631.9994(2)	630.3588(2)
eQq_{aa}	−9.349(19)	−9.686(61)	−8.183(43)	−8.798(43)
$eQq_{bb}-eQq_{cc}$	−66.445(18)	−65.774(30)	−66.347(29)	−65.814(24)

(C_5H_5) group are very small, but nonetheless determinable from the present data set. The most notable features are: (1) the ‘‘tilt’’ of the C_5H_4Cl carbon plane, with respect to the FeC_5H_5 moiety, and (2) the bending of the C–Cl bond away from the C_5H_4 moiety. This tilt angle was determined to be 1.4(5)° and the bending of the C–Cl bond was found to be 2.7(6)°. This distortion is attributed to movement of the carbon atom bonded to chlorine towards the iron atom. The C_1, C_2, C_3, C_4, and C_5 carbon atoms all lie in a common plane, to within the error limits. Figure 3 shows the molecule viewed in a direction perpendicular to the symmetry plane with the distortions exaggerated to more clearly illustrate the small deviations discussed in the above text. Other parameters derived from the structure fit are given in Table IV.

V. KRAITCHMAN ANALYSIS

Since no deuterium-substituted isotopomers have been measured thus far, the substitution (r_s) structure of chloroferrocene remains incomplete. However, coordinates for many of the atoms can be determined using a Kraitchman analysis, and the results are in good agreement with the structural parameters obtained from the least-squares fits.

The abc coordinates obtained using the Kraitchman equations are given in Table V. Nonzero and imaginary c_s coordinates obtained for atoms in the symmetry plane are due to vibrational averaging and are set to zero for the determination of internal coordinates. Since only absolute values of principal axis coordinates are obtained from this analysis, some ambiguity regarding the appropriate signs arises. However, the principal axis system is rotated significantly from the xyz system (see Fig. 3), and there is no confusion about the identification of the structure as an eclipsed conformation. The unique carbon atom, C6, in the C_5H_5 group, has a c_s coordinate signifying that it is indeed in the ab plane (within appropriate vibrational rms displacements). Assigning positive a_s and b_s values to the chlorine atom indicates that the signs of the a_s and b_s coordinates for C6 must be negative and positive, respectively, in order to obtain reasonable bond lengths and angles in this molecule. This assignment places the unique carbon atom of the C_5H_5 group ‘‘directly under’’ the unique carbon atom of the C_5H_4Cl group when viewed down the z axis. Similar comparison of the remaining carbon coordinates also shows near alignment, when observed from the perspective of a projection down the z axis. Therefore, the ligands in this molecule

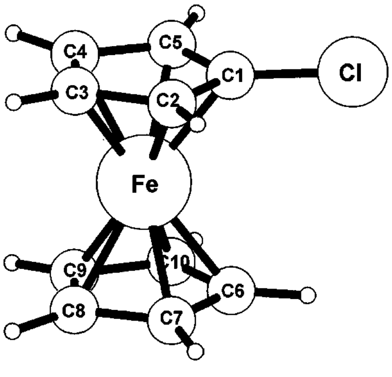

FIG. 2. Basic structure of the chloroferrocene molecule, with numbering of the carbon atoms indicated.

TABLE III. Cartesian coordinates for chloroferrocene from a least-squares fit, given in the xyz axes system. Values in Å; the estimated error limits are 0.01 Å.

Atom	x	y	z
Fe	0.000	0.000	0.000
C6	1.218	0.000	1.646
C7	0.376	1.158	1.646
C8	−0.985	0.716	1.646
C9	−0.985	−0.716	1.646
C10	0.376	−1.158	1.646
H6	2.292	0.000	1.725
H7	0.709	2.183	1.725
H8	−1.857	1.349	1.725
H9	−1.857	−1.349	1.725
H10	0.709	−2.183	1.725
C1	1.226	0.000	−1.602
C2	0.403	1.163	−1.628
C3	−0.957	0.714	−1.657
C4	−0.957	−0.714	−1.657
C5	0.403	−1.163	−1.628
Cl	2.947	0.000	−1.643
H2	0.755	2.181	−1.707
H3	−1.821	1.357	−1.736
H4	−1.821	−1.357	−1.736
H5	0.755	−2.181	−1.707

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.59.222.12 On: Thu, 27 Nov 2014 12:17:20

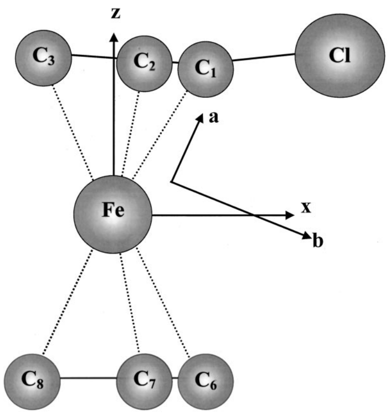

FIG. 3. The chloroferrocene molecule shown with the ab (xz) plane in the plane of the figure. Distortions of the C_5H_4Cl ligand are exaggerated to clarify the directions of angular deviations reported in Table IV. The hydrogen atoms have been omitted from the drawing to make it easier to visualize the heavy atom positions. The carbon atoms which are symmetrically displaced with respect to the ab plane are shown superimposed. The carbon atom skeletons of both cyclopentadienyl groups are planar, within experimental error limits.

are indeed ''eclipsed.'' This conclusion is also supported by the least-squares fit results, where much better fits are obtained for the eclipsed conformation. Least-squares fits performed with the ligands ''staggered'' did not converge.

Internal coordinates derived from the Kraitchman coordinates are given in Table IV. The Fe^{54} data were used to determine the Fe r_s parameters, since there was more Fe^{54} data, so better accuracy would be expected. These substitution parameters are free of the correlation problems potentially associated with the least-squares fit, and thus may provide a somewhat more reliable description of the deviations of the carbon atoms from the C_s symmetry normally exhibited by the two ligands.

TABLE IV. Internal coordinates for chloroferrocene. The sub-0 indicates least-squares fit parameters; the sub-s parameters were obtained from Kraitchman analyses. The value 108^f indicates those internal angles were fixed at 108°. ^{54}Fe data were used for Fe r_s parameters since there were more ^{54}Fe data available. The error limits on r_s parameters are 1σ.

Bond length	r_0(Å)	r_s(Å)
$r(C_1–Cl)$	1.721(12)	1.726(5)
$r(C_1–C_2)$	1.425(13)	1.422(3)
$r(C_2–C_3)$	1.433(12)	1.420(4)
$r(C_3–C_4)$	1.427(17)	1.424(3)
$r(Fe–C_1)$	2.017(10)	2.012(3)
$r(Fe–C_2)$	2.041(8)	2.039(4)
$r(Fe–C_3)$	2.042(10)	2.050(7)
$r(C_6–C_7)$	1.432(5)	1.427(2)
$r(C_7–C_8)$	1.432(5)	1.430(2)
$r(C_8–C_9)$	1.432(5)	1.425(3)
$r(Fe–C_6)$	2.048(5)	2.040(7)
$r(Fe–C_7)$	2.048(5)	2.048(5)
$r(Fe–C_8)$	2.048(5)	2.055(5)
Interbond angle	$\angle_0$(°)	$\angle_s$(°)
$\angle(C_5C_1C_2)$	109.4(14)	109.1(3)
$\angle(C_1C_2C_3)$	107.0(9)	107.1(3)
$\angle(C_2C_3C_4)$	108.3(6)	108.3(3)
$\angle(C_{10}C_6C_7)$	108^f	107.6(3)
$\angle(C_6C_7C_8)$	108^f	108.3(3)
$\angle(C_7C_8C_9)$	108^f	107.9(3)
C–Cl ''bend''	2.7(6)	4.1(5)
C_5H_4 ''tilt''	1.43(8)	2.2(4)

TABLE V. Substitution coordinates in the principal axis system of the parent isotopomer for chloroferrocene, obtained from the Kraitchman analyses. The parent isotopomer is $^{56}Fe^{12}C_{10}{}^{1}H_9{}^{35}Cl$. Values in Å; the estimated error limits are 0.01 Å (2σ).

Atom substituted	$\lvert a_s\rvert$	$\lvert b_s\rvert$	$\lvert c_s\rvert$
^{54}Fe	0.477	0.200	0.011
^{57}Fe	0.477	0.193	0.061
^{37}Cl	2.636	1.073	$0.007i$
$^{13}C_1$	1.531	0.250	0.040
$^{13}C_2$	1.039	0.914	1.158
$^{13}C_3$	0.227	1.990	0.712
$^{13}C_6$	1.012	1.772	$0.101i$
$^{13}C_7$	1.542	1.118	1.152
$^{13}C_8$	2.391	0.055	0.712

VI. CONCLUSIONS

A nearly complete gas-phase structure of chloroferrocene has now been obtained from spectroscopic data. The present data set containing multiple chlorine, iron, and carbon isotopomers provides heavy atom parameters to sufficient precision to discern small structural details associated with distortions of the C_5H_4Cl ligand. Analysis of the substitution coordinates indicates that the two ligands are eclipsed. Distortions of the halogenated cyclopentadienyl ligand are clearly much larger than any distortions of the unsubstituted cyclopentadienyl ligand. The carbon skeletons for both cyclopentadienyl ligands are planar, within the error limits. Distortions of the unsubstituted cyclopentadienyl ligand are not larger than the estimated experimental errors.

ACKNOWLEDGMENTS

We are very grateful to the National Science Foundation (Grant No. CHE-9634130) for support of this research. We thank Dr. Oliver Indris for help with the data and figures.

[1] R. F. Bryan and A. J. Leadbetter, A.C.A. (Winter) **14**, 28 (1986).
[2] B. J. Drouin, P. A. Cassak, and S. G. Kukolich, Inorg. Chem. **36**, 2868 (1997).
[3] L. Phillips, A. R. Lacey, and M. K. Cooper, J. Chem. Soc., Dalton Trans. **5**, 1383 (1988).
[4] A. Houlton, J. R. Miller, R. M. G. Roberts, and J. Silver, J. Chem. Soc., Dalton Trans. **3**, 467 (1991).
[5] L. Korecz, H. Abou, G. Ortaggi, M. Graziani, U. Belluco, and K. Burger, Inorg. Chim. Acta **9**, 209 (1974).
[6] T. Vondrak, J. Organomet. Chem. **93**, 275 (1984).
[7] S. Barfuss, K. H. Emrich, W. Hirschwald, P. A. Dowben, and N. M. Boag, J. Organomet. Chem. **391**, 209 (1990).
[8] R. Epton, G. Marr, and G. K. Rogers, J. Organomet. Chem. **150**, 93 (1978).
[9] E. G. Perevalova, Organometal. Reac. **4**, 306 (1972).
[10] B. J. Drouin, T. G. Lavaty, P. A. Cassak, and S. G. Kukolich, J. Chem. Phys. **107**, 6541 (1997).
[11] E. Rosenthal and B. P. Dailey, J. Chem. Phys. **43**, 2093 (1965).
[12] R. L. Poynter, J. Chem. Phys. **39**, 1962 (1963); W. Caminati and A. M. Mirri, Chem. Phys. Lett. **12**, 127 (1971).
[13] H. M. Pickett, J. Mol. Spectrosc. **148**, 371 (1991) [see also http://spec.jpl.nasa.gov/].

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.59.222.12 On: Thu, 27 Nov 2014 12:17:20