Organic and Biological Chemistry

The Organic Solid State. V. Symmetry Distortions in Ferrocenium Compounds[1]

D. O. Cowan,*[2] G. A. Candela,[3] and F. Kaufman[4]

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, and National Bureau of Standards, Washington, D. C. *Received October 26, 1970*

Abstract: The magnetic susceptibilities of biferrocene [Fe(II)Fe(III)] picrate (**1**) and biferrocene [Fe(III)Fe(III)] difluoroborate (**2**) were determined from 2 to 300°K. The experimental curves for the effective magnetic moment (μ_{eff}) are compared with theoretical curves based on a model involving molecular distortion from axial symmetry. For compound **1**, in the temperature range 77–300°K, the best-fit temperature-independent distortion factor (δ = 1000 cm^{-1}/ferrocenium unit) is large when compared to previously observed distortions. The deviation from the theoretical μ_{eff} curve for this compound is small. For compound **2** in the temperature range 77–300°K the best-fit temperature-independent distortion factor is 750 cm^{-1}/ferrocenium unit; while in the temperature range 2–4°K the distortion factor is considerably smaller (δ = 150 cm^{-1}/ferrocenium unit). The electron spin resonance spectra of compounds **1** and **2** were measured at 77 and 298°K. The observed g values were used to calculate the effective magnetic moments and the distortion factors for compounds **1** and **2**. These values are in good agreement with those obtained from the magnetic susceptibility measurements. The observed low-temperature collapse of the g_x, g_y signal and the appearance of a new g_z signal (compound **2**) are consistent with a large reduction in the distortion parameter at low temperature.

Although ferrocene has been the subject of a large number of theoretical and experimental investigations since its discovery in 1951,[5] it has not been until recently that exact details of its electronic structure have become available. The visible transition of ferrocenium ion at 15,733 cm^{-1} was originally[6] thought to involve excitation from the $^2E_{2g}[(a_{1g})^2(e_{2g})^3]$ ground state to the first excited state, $^2A_{1g}[(a_{1g})^1(e_{2g})^4]$. This absorption band, however, has been shown[7] to be a charge-transfer transition from the highest occupied ligand orbital (e_{1u}) to the metal. Consequently, the energy of the $^2A_{1g}$ state of ferrocenium ion is not well known.

In the first detailed study[8] of the magnetic susceptibility of a series of ferrocenium compounds, significant deviations from theoretical behavior were observed. It was shown that a temperature-dependent low-symmetry crystal field change *or* thermal population of the $^2A_{1g}$ state could account for the experimental data.

Electron spin resonance studies could shed considerable light on these questions, but unfortunately all of the esr studies have been limited to low-temperature measurements on ferrocenium salts[7a] (20°K in a glass) or on the analogous Fe(III) dicarbollide compounds[9] (85°K). Theory[9] and experiment[7a] suggest that the short relaxation time T_1 in these compounds makes it difficult to observe esr signals at high temperature.

However, since it is known[10] that substitution in these compounds primarily influences the symmetry of the molecule, it is reasonable to assume that a highly unsymmetric ferrocenium salt should show a large splitting of the Kramer's doublets. This increased splitting of states should result in longer esr relaxation times.

An account of the synthesis and physical properties of some salts of biferrocene have recently appeared.[11] Here, we wish to report the results of an electron spin resonance and magnetic susceptibility study of these compounds. The experimental data bear directly on the question of the position of the first excited state and on the importance of symmetry distortions in ferrocenium compounds.

Experimental Section

The materials used in this study, biferrocene Fe(II)Fe(III) picrate (**1**) and biferrocene Fe(III)Fe(III) fluoroborate (**2**), have been characterized by a variety of physical techniques.[11d] The picrate salt was recrystallized several times from methanol–water mixtures and dried under high vacuum. The fluoroborate salt was purified by precipitation from nitromethane solutions by the addition of diethyl ether.

All paramagnetic resonance measurements were made on a Varian E-12 epr spectrometer with 100-kHz field modulation. The instrument's calibration was checked against DPPH and agreement

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[1] The Organic Solid State. IV. See D. O. Cowan, F. Kaufman, and R. Collins, *J. Phys. Chem.*, 75, 2025 (1971).

[2] Author to whom inquiries should be addressed at J. H. U.; A. P. Sloan Fellow.

[3] National Bureau of Standards.

[4] Taken from the Ph.D. Thesis of F. Kaufman submitted to J. H. U.; National Institutes of Health Predoctoral Fellow.

[5] M. Rosenblum, "Chemistry of the Iron Group Metallocene," Wiley, New York, N. Y., 1965.

[6] D. A. Levy and L. E. Orgel, *Mol. Phys.*, 4, 93 (1961); D. R. Scott and R. S. Becker, *J. Phys. Chem.*, 69, 3207 (1965).

[7] (a) R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, 91, 4929 (1969); (b) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *ibid.*, 92, 3233 (1970).

[8] We thank Professor H. B. Gray for providing us with a copy of his manuscript prior to its publication.

[9] A. H. Maki and T. E. Berry, *J. Amer. Chem. Soc.*, 87, 4437 (1965).

[10] Personal communication from R. Prins.

[11] (a) D. O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.*, 92, 219 (1970); (b) F. Kaufman and D. O. Cowan, *ibid.*, 92, 6198 (1970); (c) D. O.Cowan, F. Kaufman, and R. L. Collins, *J. Phys. Chem.*, in press; (d) the results of the elemental analyses and uv, infrared, and Mössbauer spectra confirm our assignment of structure and valence states.

Table I

	Temp, °K	$g_{\parallel}$	$\lvert g_{\perp}\rvert$	$\mu_{eff}{}^{c}$	$\mu_{eff}{}^{d}$	$\lvert\zeta\rvert$	k'	$\lvert\delta\rvert^{e}$	$\lvert\delta\rvert^{h}$
Biferrocene(3,3)$(BF_4)_2$ (s)[b]	298	3.2	1.91	3.42	3.53	0.74	1.0	660	750
Biferrocene(2,3) picrate (s)	77	$\bar{g} = 2.42$		2.10	2.21			985	1000
Biferrocene(2,3) picrate (s)[a]	77	3.53	1.85	2.18	2.23	0.67	1.0		
$(C_6H_5C_5H_4)_2Fe^+$ [a,f]	20	3.62	1.75			0.58	0.82	580[g]	
$(C_5H_5)_2Fe^+$ [a,f]	20	4.35	1.26			0.36	0.76	270	

[a] Frozen solution. [b] See text for 77°K. [c] Determined from $\mu = [(g_{\parallel}^2/3 + 2g_{\perp}^2/3)S(S + 1)^{1/2}$. [d] From direct measurement. [e] Units of cm^{-1} per ferrocenium unit. [f] *Cf.* ref 7. [g] *Cf.* ref 13. [h] Best fit from theoretical susceptibility.

was found to be within 0.1%. Measurements were done at 298 and 77°K on polycrystalline solids or on frozen glasses of the compounds in acetone. Samples were maintained at 77°K by a bath of liquid nitrogen.

The magnetic susceptibility of the samples was determined in the range 2–298°K by a modified Faraday method. The apparatus has been previously described.[12] The measurements were run with the samples cooled by a heat exchange gas (He or N_2). The temperatures above 77°K were measured with a calibrated copper–constantan thermocouple. In the 2–4°K range, the temperature was determined from the vapor pressure of the liquid He used as the coolant. Corrections were always made for the sample container and for the diamagnetism of the materials. The corrections for picrate and fluoroborate[8] anion and for biferrocenyl[13] were determined by direct measurement.

Results

Esr Measurements. Electron spin resonance signals were recorded at 78 and at 298°K. Both compounds showed a polycrystalline line shape that could be fitted with an axial g tensor (see Figure 1 and 2). The observed $g_{\parallel}$ and $g_{\perp}$ values are given in Table I along with the calculated values of the orbital reduction factor (k'), the splitting of the energy levels due to symmetry distortion (δ), and the wave function mixing parameter that results from this departure from axial symmetry (ζ). These constants were determined by use of the theoretical g value expressions derived by Maki and Berry[9]

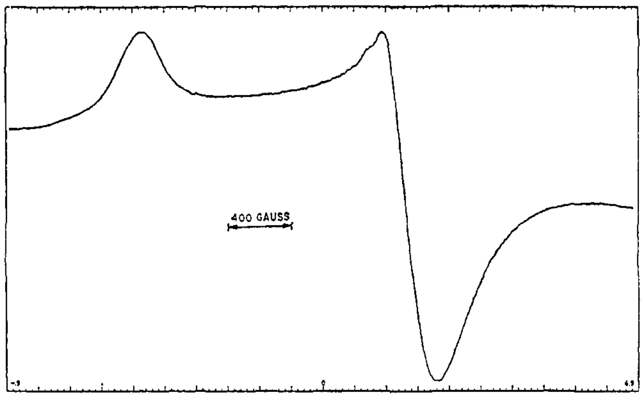

Figure 1. Electron spin resonance signal of biferrocene Fe(II)-Fe(III) picrate in acetone (77°K). Zero is 3000 G.

$$g_{\perp} = 4\zeta/(1 + \zeta^2)$$

$$g_{\parallel} = 2 + 4k'(1 - \zeta^2)/(1 + \zeta^2)$$

$$|\zeta| = x/[1 + (1 + x^2)]^{1/2}$$

$$|x| = \delta/k'\xi$$

where ξ is the spin–orbital coupling constant.

In contrast to other ferrocenium salts,[7a] the biferrocene Fe(II)Fe(III) picrate exhibited a strong, well-resolved signal in a glass kept at 78°K. No absorptions in the solid state or in solutions at 298° could be detected, but samples of the polycrystalline solid did exhibit a broad unresolved signal at the lower temperatures used. The effective magnetic moments, μ_{eff}, calculated from these g values, ($\mu_{eff} = [{}^1/_3(g_{\parallel}{}^2 + 2g_{\perp}{}^2)S(S + 1)]^{1/2}$, were found to be in excellent agreement with the values determined by direct magnetic measurements (see Table I). The value of δ (cm^{-1}/ferrocenium unit) in this compound is noteworthy because it is substantially larger than the value found for other ferrocenium derivatives or carborane ferrocenium[9] analogs that have been studied. Presumably, the ferrocene substituent has strongly distorted the $Fe(Cp)_2{}^+$ from its expected D_5 symmetry. One consequence of this is that the splitting between the two Kramer's doublets has been greatly increased. This results in a reduction in the expectation values due to the spin–orbit and orbital momentum operators for the wave functions of the orbitally degenerate configuration ${}^2E_{2g}[(a_{1g})^2(e_{2g})^3]$. As a consequence, the relaxation time T_1 is made longer and the absorption becomes detectable at higher temperatures.

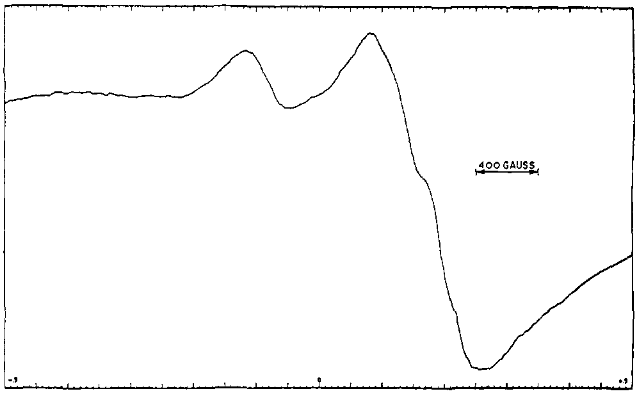

Figure 2. Electron spin resonance signal of biferrocene Fe(III)-Fe(III) fluoroborate(s) (298°K). Zero is 3000 G.

The esr spectrum of the polycrystalline[14] (3,3) compound was observed at 298°K (Figure 2). In addition, an apparent absorption was observed in the center of the $g_{\perp}$ peak. This signal was not a function of the purity of the material since all samples of the (3,3) salt investigated showed this splitting. The peak could not be resolved over a wide range of field and amplitude modulation values. We therefore assign this signal to the $g_x \neq g_y$ values for the (3,3) cation. Though second-

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(12) G. A. Candela and R. E. Mundy, *Rev. Sci. Instr.*, 36, 338 (1965).

(13) *Cf.* ref 5, p 34.

(14) No experiments with the (3,3) compound in solution were performed because it is known (*cf.* ref 11) that this material is irreversibly reduced to the (2,3) cation in fluid media.

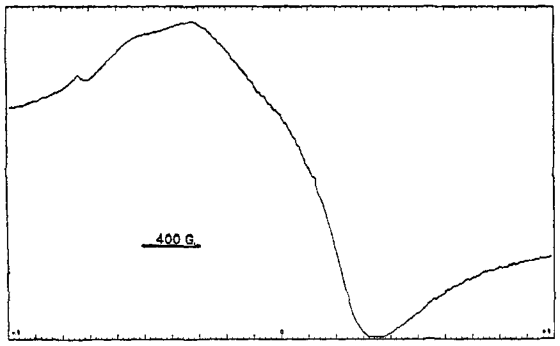

Figure 3. Electron spin resonance signal of biferrocene Fe(III)-Fe(III) fluoroborate(s) (77°K). Zero is 3000 G.

order calculations predict that these low-symmetry compounds should exhibit an esr spectrum with $g_x \neq g_y$, this splitting was presumably not seen in the earlier studies at low temperature because of the lower distortions and larger g tensor anisotropies involved.

At liquid nitrogen temperatures, it was observed that the spectrum of the (3,3) salt had undergone a drastic change (Figure 3). The width of the $g_{x,y}$ peak had more than doubled and the g_z peak had become almost unresolved. In addition, a new absorption was observed at $g = 4.35$ (see Discussion). By subjecting the sample to several freeze–thaw cycles, we found that these changes in the spectrum were reversible.

Magnetic Susceptibility. The magnetic susceptibilities of the materials were determined in the temperature range 2–298°K. The results are shown in Figures 4 and 5, where the measured susceptibilities are plotted[15] as effective magnetic moment *vs.* temperature. The temperature dependence of the (2,3) compound is qualitatively similar to the behavior exhibited by a series of substituted and unsubstituted ferrocenium salts.[7b,8] The (3,3) compound, on the other hand, exhibits a sharp increase in moment at the lower temperature studied. Whereas it is possible to attribute this behavior to impurities in the sample, the data above 78°K give no indication of the presence of other species. *There is excellent agreement between the μ_{eff} calculated from esr and from direct measurement.* In addition, the Mössbauer spectrum[11c] of the (3,3) compound at 78 and 298°K indicates that just one type of iron atom is present. The esr at liquid nitrogen temperature also indicates a drastic intrinsic change in the total character of the system as a function of decreasing temperature. We will show that the observed collapse of the g_x,g_y signal and the appearance of a new g_z signal at lower fields are consistent with a reduction in the distortion parameter δ of the system, with the result that the molecule becomes more axially symmetric at low temperatures.

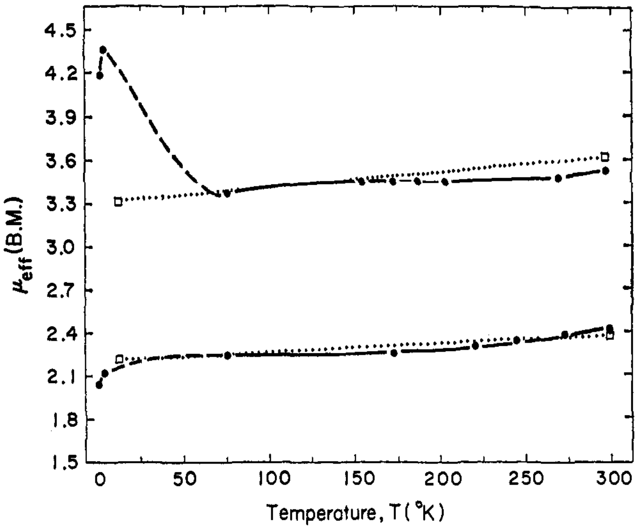

Figure 4. Curves of the effective magnetic moment, μ_{eff}, for biferrocene salts. The dotted lines are theoretical curves for a $^2E_{2g}$ ground state experiencing a low-symmetry crystal field (δ). The upper curve is biferrocene Fe(III)Fe(III) fluoroborate (δ = 750 cm^{-1}); the bottom curve is biferrocene Fe(II)Fe(III) picrate (δ = 1000 cm^{-1}).

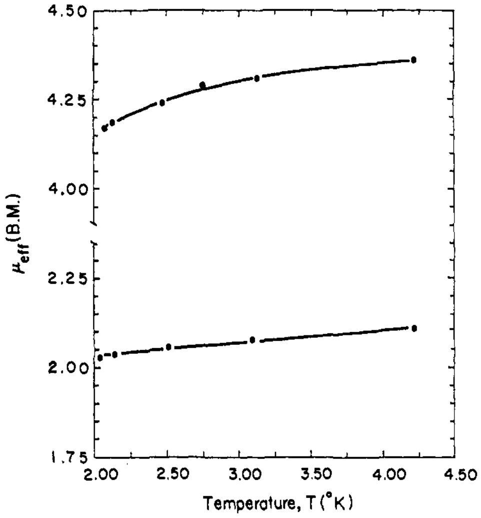

Figure 5. Curves of the effective magnetic moment, μ_{eff}, for (upper curve) biferrocene Fe(III)Fe(III) fluoroborate and (lower curve) biferrocene Fe(II)Fe(III) picrate.

Discussion

Magnetic Behavior. Theory *vs.* Experiment. Gray[7b,8] has derived the theoretical expression for the temperature dependence of the magnetic susceptibility. He employed the wave functions[9] for the two Kramer's doublets of the $^2E_{2g}$ ground state as a basis set in Van Vleck's formula[16] for the susceptibility. The equations for χ and μ are given.

$$\chi_{\|}(E'') = \frac{N\beta^2}{kT}\left[\left(1 + \frac{2k'(1-\zeta^2)}{(1+\zeta^2)}\right)^2 + \frac{16\zeta^2k'^2(kT)}{(\zeta^2+\delta^2)^{1/2}(1+\zeta^2)^2}\right]$$

$$\chi_{\perp}(E'') = \frac{N\beta^2}{kT}\left[\frac{4\zeta^2}{(1+\zeta^2)^2} + \frac{2kT(1-\zeta^2)^2}{(1+\zeta^2)^2(\xi^2+\delta)^{1/2}}\right]$$

$$\chi = 1/3(\chi_{\|} + 2\chi_{\perp})$$

$$\mu_{eff} = 2.828(\chi T)^{1/2}$$

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(15) The magnetic results were plotted as $\mu_{eff} = 2.83\sqrt{\chi T}$ rather than as μ^2 or χT to facilitate comparison with the other data available on this system (*cf.* ref 7b).

(16) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932; B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 248.

The theoretical curves for a temperature-independent δ are plotted[17] in Figure 3. For the (2,3) compound, the deviations from the calculated behavior are very similar to those found for ferrocenium compounds with smaller distortion parameters.[8] The extent of deviation, however, is less dramatic since the effect of a higher δ is to decrease the temperature dependence of the theoretical susceptibility. Gray has elegantly demonstrated that the thermal population of the $^2A_{1g}$ state *or* a low-symmetry crystal field, $\delta(T)$, which varies with temperature, leads to a magnetic moment expression that is consistent with experimental results. It is reasonable to assume that one of these mechanisms gives rise to the temperature-independent μ_{eff} observed in the biferrocene systems.

The physical behavior of the (3,3) compound is uncomplicated at temperatures greater than 78°K, but there is an increase in the magnetic moment of $\simeq 33\%$ in the 2–4°, region. Because of the low temperatures involved, this change is not likely to be due to depopulation of an excited state. Even at room temperatures there is no evidence for a populated $^2A_{1g}$ state. Only esr absorptions due to the $^2E_{2g}$ configuration can be detected, and the anisotropic g values obtained give better agreement with the magnetic data than a system with $\Delta E[^2A_{1g} - {}^2E_{2g}] \simeq 200\ \text{cm}^{-1}$ would show.[18]

The experimental magnetic susceptibility data can be explained by proposing that the (3,3) compound, which is highly distorted at high temperatures, becomes more axially symmetric as it is cooled. In this interpretation, the symmetry changes in the system begin to appear near 78°K, where the esr spectrum (Figure 3) shows the predicted[9] collapse of $g_\perp$ and the increase in $g_{\|}$ as the molecule relaxes to more rigorous D_5 geometry. The size of the reduction in δ can be evaluated from the susceptibility at low temperature. Excellent agreement with theory[19] is predicted if the (3,3) compound has a $\delta = 150\ \text{cm}^{-1}$ at 4°K. This change (δ = 750–150) represents a fivefold reduction in the symmetry parameter ($\delta = 750$) determined from the best fit to the 78–300°K magnetic data.

It is important to understand how the behavior of this compound is related to the less distorted parent ion. The changes in the esr and in μ_{eff} and the inability to detect $^2A_{1g}$ populations might solely be a function of the large doublet splitting in the (3,3) compound. On the other hand, it is possible that the first excited state in ferrocenium compounds is relatively unaffected by substitution because it lies well above the ground state. This would mean that a temperature-dependent δ, so dramatically demonstrated by the (3,3) compound, is in fact intrinsic to the dicyclopentadienyliron(III) system.

The Size of $\Delta E(^2A_{1g} - {}^2E_{2g})$. Mössbauer spectroscopy and photoelectron spectroscopy are two experimental techniques that provide a measure of the energy of the $^2A_{1g}$ state in ferrocenium compounds. In the Mössbauer experiment, the quadrupole splitting is expected to be dependent on thermal excitation from ground to excited states.[20] This is because the electric field gradient, V_{zz}, is dependent on the number, distance, and orientation of d electrons about the ^{57}Fe nucleus. The ferrocenium ion has an electronic structure that leads to a highly symmetrical electrostatic field about the iron atom. As a result, the quadrupole splitting in $Fe(Cp)_2^+$ compounds cannot be resolved (<0.1 mm/sec).[21] The neutral ferrocene molecule, on the other hand, has a large quadrupole splitting (2.4 mm/sec), which is easily detectable at room temperature. Collins[22] has shown that the molecular orbital scheme for ferrocene can be used to calculate the change in V_{zz} and the resulting collapse of the quadrupole splitting in the oxidized species. This analysis can be used to show that the $^2A_{1g}$ state of ferrocenium ion has an electric field gradient that is positive and substantially larger than zero. If one writes an expression for the quadrupole splitting due to contributions from the $^2E_{2g}$ *and* $^2A_{1g}$ electronic states, it can readily be seen that any appreciable population of the latter state would lead to a temperature-*dependent* quadrupole splitting. Since it is known[21,22] that these splittings are virtually independent of temperature in $Fe(Cp)_2^+$ salts, it is reasonable to assume that there are no low-lying excited states in these materials which involve appreciable 3d electron density.[23]

The results of the photoelectron experiments on $(C_5H_5)_2Fe$ bear directly on the question of the energy of the excited states in ferrocenium ion. The lowest energy peaks in the spectrum at 6.85 and 7.2 eV have been assigned[7a,24] to the $Fc(^1A_{1g}) \rightarrow Fc^+(^2E_{2g})$ and $Fc(^1A_{1g}) \rightarrow Fc^+(^2A_{1g})$ transitions, respectively, on the basis of the intensity and shape of the observed photoelectron bands. Subtraction of these two ionization potentials gives[7a] an energy of 0.35 eV (2800 cm^{-1}) for the $^2A_{1g} \rightarrow {}^2E_{2g}$ transition in the ferrocenium ion. No real agreement of this value with experiment was expected, because it was thought that the dimensional changes in going from ferrocene to its ion were significant. We have pointed out previously[11b] that the bond length differences between $Fe(Cp)_2$ and $Fe(Cp)_2^+$ were negligible. As a result, photoelectron spectroscopy may provide accurate state energies for the ferrocenium ion. Subtraction of the first ionization potential from the third ionization potential gives an energy of 1.95 eV (15,700 cm^{-1}), which was assigned[24b] to the $^2E_{2g} \rightarrow {}^2E_{1u}$ transition. This energy is in excellent agreement with the results of Gray,[7b] who placed the origin (0,0) of this ligand to metal transition at 15,733 cm^{-1} on the basis of the absorption spectrum (77°K) of ferrocenium fluoroborate in 10 *M* KCl. In light of the above agreement, it is doubtful that the photoelectron results for the $^2A_{1g}$, $^2E_{2g}$ splitting could be in error by as much as an order of magnitude. Therefore, the available evidence from photoelectron spectroscopy can be interpreted to mean that the $^2A_{1g}$ state is higher than 300 cm^{-1} and may be as high as 3000 cm^{-1} above the ground state. The evi-

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(17) A k' value of 1, determined from the esr experiments, was used. The spin–orbit coupling constants were assumed to be unaffected by the presence of another iron atom in the molecule.

(18) A splitting of this size would lead to considerable configuration interaction between the nearly degenerate states (*cf.* ref 9). The g values and derived data from the esr are not consistent with another distortion parameter, $\epsilon = \langle e_{2g} \pm |H'|a_{1g}'\rangle$, arising in this manner.

(19) Because of the polycrystallinity and high magnetic moment of the sample at these low temperatures, substantial anisotropies due to preferential orientation in the magnetic field are expected. For a $\delta = 150\ \text{cm}^{-1}$, less than 8% of the molecules are so affected.

(20) G. Lang, *Quart. Rev. Biophys.*, 3, 1 (1970).

(21) G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, 38, 2106 (1963).

(22) R. L. Collins, *ibid.*, 42, 1072 (1965).

(23) The Mössbauer results on the (2,3) and (3,3) compounds have recently been reported (*cf.* ref 11c) and they are in complete agreement with the temperature independence observed in unsubstituted ferrocenium salts.

(24) (a) D. W. Turner in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968, p 102; (b) R. Prins, *Chem. Commun.*, 280 (1970).

dence from this technique and from Mössbauer spectroscopy supports a model in which the $^2E_{2g}$ state is the only populated state in ferrocenium compounds.

Distortions from D_5 Symmetry in Ferrocene Compounds. Crystallographic data on ferrocene[25] and biferrocene[26] suggest that the iron atom in these compounds is not bonded equally to all five carbon atoms in each ring. These deviations from fivefold symmetry result in esr g values for the corresponding ferrocenium salts that are far removed from the results expected for a rigorously axial system. It thus seems probable that the observed variations[25,26] in bond distances are significant and are not a result of systematic errors.

Though no drastic changes in the unit cell constants were detected in low-temperature crystallographic studies[27] of ferrocene (95°), there exists a body of evidence which indicates that these compounds undergo changes in configuration as a function of temperature. Crystals of ferrocene disintegrate violently when cooled to liquid nitrogen temperatures.[27] In addition, there is a λ point transition[27] in the heat capacity curve and a region of anomalous narrowing[28] in the line width of the proton magnetic resonance signal in the temperature range 115–225°K. Neutron diffraction measurements[29] show that in crystals of ferrocene the molecules exist in a number of energetically distinct conformations due to a variety of intra- and intermolecular interactions. Several authors[27,28,30] have proposed that as a crystal of ferrocene is cooled, the high energy (eclipsed) conformations of the molecule relax to the more stable (staggered) conformations, and the crystal becomes ordered below the λ point. Since the eclipsed ring conformation has been shown to cause distortions in the parallel sandwich structure of certain bridged ferrocenes,[31,32] it would be expected that below the region of the λ point transition (<115°K), the molecules in the crystal would be more nearly D_{5d} in character. Though no real coincidence is expected in comparison of the symmetry properties of ferrocenium ion with that of its parent, it should be noted that the magnetic susceptibility data[7b] show a transition that may correspond to a relatively constant symmetry parameter δ below a temperature of 110°K. The coincidence with the line broadening data of ferrocene may mean that the important interactions in the solid state are of intramolecular character, and that differences in crystal structure have little effect on the reordering process. Support for this picture is provided by the structural data on biferrocenyl,[30] which indicate that the C–C bridge has made the ring planes nonparallel (2.8° deviation) and has resulted in a conformation which is midway (17°) between the eclipsed (0°) and fully staggered (36°) positions. This conformation results in a room temperature distortion parameter which is significantly larger (see esr section) than the monoferrocenyl systems studied. In addition, the ferrocene substituent has a marked effect on the temperature range of the nmr line width narrowing. The second moments and line width[33] stay almost constant down to 78°K where they increase very rapidly with increasing temperature. As in the case of ferrocene, these sudden changes again may indicate that below 78°K there are conformational and symmetry changes in the molecule.

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(25) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956).

(26) A. C. MacDonald and J. Trotter, *ibid.*, **17**, 872 (1964).

(27) J. H. Edwards, G. L. Kington, and R. Mason, *Trans. Faraday Soc.*, **56**, 660 (1960).

(28) L. N. Mulay and A. Attalla, *J. Amer. Chem. Soc.*, **85**, 702 (1963).

(29) B. T. Willis, AERE Report (Harwell) R3708, 1961.

(30) A. Haaland and J. E. Nelsson, *Acta Chem. Scand.*, **22**, 2653 1968).

(31) *Cf.* ref 9, p 29.

(32) Some ferrocenium salts begin to show increases in the μ_{eff} at 250°. These could be due to discontinuous decreases in δ since the line broadening data indicates the onset of that process at 225°K.

(33) Data given for diferrocenylmercury.