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California Institute of Technology, Pasadena, California 91109

Magnetic Susceptibility Study of Various Ferricenium and Iron(III) Dicarbollide Compounds

By DAVID N. HENDRICKSON, Y. S. SOHN, and HARRY B. GRAY*

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The ground electronic state $[{}^2E_{2g}(a_{1g})^2(e_{2g})^3]$ of the ferricenium ion has been further characterized by a variable-temperature (40–300°K) magnetic susceptibility study of nine ferricenium and two analogous iron(III) dicarbollide ($1,2\text{-}B_9C_2H_{11}{}^{2-}$) compounds. The observed temperature independence of the effective magnetic moments for these ferricenium compounds is explicable in terms of either a temperature-dependent, low-symmetry crystal field distortion (external and/or internal) or thermal population of the ${}^2A_{1g}(a_{1g})^1(e_{2g})^4$ state. Solvent and counterion effects on the magnetic properties of the ferricenium ion are appreciable.

Introduction

The electronic structure of the ferricenium ion has been a subject of continuing interest. Theoretical molecular orbital investigations[1,2] have provided some insight into the bonding of the ferricenium ion but are not reliable as a means of characterizing the fine details of the ground and lowest electronic states. Unfortunately, the electronic absorption spectrum of the ferricenium ion is complicated[3-5] and to date has yielded little detailed electronic structural information.

The esr studies of ferricenium compounds by Prins and Reinders[6] and analogous iron(III) dicarbollide compounds by Maki and Berry[7] have been of greatest value in elucidating the ground electronic configuration of these systems. Both of these low-temperature esr studies have indicated, on the basis of a highly anisotropic g tensor, that the ground state of the ferricenium ion is a ${}^2E_{2g}(a_{1g})^2(e_{2g})^3$ state which is split into two Kramers doublets by spin–orbit coupling and crystal fields of symmetry lower than D_5. Here the spin–orbit interaction and low-symmetry distortion were found by an analysis of their data to be comparable in magnitude. Contrary to these reports, Saito[8] has obtained an essentially isotropic g tensor for a species believed to be ferricenium ion produced by γ irradiation of ferrocene. In connection with Saito's report it is of interest that German and Dyatkina[9] have demonstrated theoretically that a nearly isotropic g tensor would result if the ferricenium ion were experiencing a large Jahn–Teller distortion ($\sim$13 times the spin–orbit interaction).

We have recently communicated[5a] certain results of variable-temperature magnetic susceptibility studies which further characterize the ${}^2E_{2g}$ ground state of the ferricenium ion. In this paper we will expand on this communication; new magnetic susceptibility data will be presented for some substituted ferricenium compounds as well as for two iron(III) dicarbollide compounds. A brief discussion of the effects of ring substitution and anion environment on the magnetic properties of the ferricenium ion will be given.

Experimental Section

Compound Preparations.—Ferrocene (Eastman Kodak) was purified by recrystallization from ethanol, followed by sublimation. Chemically pure (Research Inorganic Chemicals) mono- and 1,1′-dibutylferrocene were used without further purification. Phenylferrocene was synthesized by Broadhead and Pauson's recipe[10] and recrystallized from n-hexane (mp 111°, lit. mp 109–110°). All other chemicals were reagent grade unless specified. All chemical analyses were performed by Schwarzkopf Microanalytical Laboratory.

Samples of $\mathbf{[Fe(C_5H_5)_2]I_3}$, $\mathbf{[Fe(}n\mathbf{\text{-}C_4H_9C_5H_4)(C_5H_5)]I_3}$, and $\mathbf{[Fe(C_6H_5C_5H_4)(C_5H_5)]I_4}$ were prepared by mixing 1 mmol of ferrocene or substituted ferrocene with 2.5 mmol of iodine, both dissolved in cyclohexane. The resulting dark red precipitate was recrystallized from nitromethane. *Anal.* Calcd for $[Fe(C_5H_5)_2]I_3$: Fe, 9.85; I, 67.17. Found: Fe, 9.66; I, 67.52. Calcd for $[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)]I_3$: Fe, 8.97; I, 61.12; C, 27.00; H, 2.91. Found: Fe, 9.18; I, 61.11; C, 26.64; H, 2.95. Calcd for $[Fe(C_6H_5C_5H_4)(C_5H_5)]I_4$: Fe, 7.26; I, 65.95; C, 24.36; H, 1.83. Found: Fe, 7.36; I, 63.86; C, 24.36; H, 2.11.

Samples of $\mathbf{[Fe(C_5H_5)_2](C_6H_2N_3O_7)}$ and $\mathbf{[Fe(}n\mathbf{\text{-}C_4H_9C_5H_4)}$-

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[1] For ferricenium MO treatment: E. M. Shustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **144**, 141 (1960).

[2] For ferrocene MO treatments: D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961), and references therein; J. P. Dahl and C. J. Ballhausen, *Kgl. Dan. Vidensk. Selsk., Mat. Fys. Medd.*, **33**, No. 5 (1961); R. D. Fischer, *Theor. Chim. Acta*, **1**, 418 (1963); A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *J. Chem. Phys.*, **47**, 1104 (1967); J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, **1**, 462 (1967).

[3] D. A. Levy and L. E. Orgel, *Mol. Phys.*, **4**, 93 (1961).

[4] D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **69**, 3207 (1965).

[5] (a) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 3233 (1970); (b) R. Prins, *Chem. Commun.*, 280 (1970).

[6] R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, **91**, 4929 (1969).

[7] A. H. Maki and T. E. Berry, *ibid.*, **87**, 4437 (1965).

[8] E. Saito, *J. Chem. Phys.*, **50**, 3539 (1969).

[9] E. D. German and M. E. Dyatkina, *Zh. Strukt. Khim.*, **6**, 898 (1965).

[10] G. D. Broadhead and P. S. Pauson, *J. Chem. Soc.*, 367 (1955).

$(C_5H_5)](C_6H_2N_3O_7)$ were prepared using the method of Pavlik and Klikorka.[11] Ferricenium picrate could also be made by mixing 1 mmol of ferrocene in 50 ml of benzene with 30 ml of benzene in which 2 mmol of *p*-benzoquinone and a large excess of picric acid had been dissolved. *Anal.* Calcd for $[Fe(C_5H_5)_2](C_6H_2N_3O_7)$: Fe, 13.47; C, 46.40; N, 10.15; H, 2.92. Found: Fe, 13.67; C, 46.11; N, 10.33; H, 3.05. Calcd for $[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)](C_6H_2N_3O_7)$: Fe, 11.88; C, 51.08; N, 8.94; H, 4.29. Found: Fe, 11.72; C, 51.29; N, 8.67; H, 4.26.

The hexafluorophosphates **$[Fe(C_5H_5)_2]PF_6$**, **$[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)]PF_6$**, and **$[Fe(n\text{-}C_4H_9C_5H_4)_2]PF_6$** were prepared from ferricenium sulfate solution by precipitation with a fourfold excess of $(NH_4)PF_6$ dissolved in a minimum of water. The resulting precipitates were dried over P_4O_{10}. Ferricenium hexafluorophosphate could also be made by mixing concentrated solutions of ferricenium tetrafluoroborate and ammonium hexafluorophosphate. *Anal.* Calcd for $[Fe(C_5H_5)_2]PF_6$: Fe, 16.87; C, 36.29; F, 34.44; H, 3.05. Found: Fe, 16.88; C, 36.23; F, 34.17; H, 3.07. Calcd for $[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)]PF_6$: Fe, 14.43; C, 43.44; F, 29.45; H, 4.69. Found: Fe, 14.57; C, 43.20; F, 29.34; H, 4.53. Calcd for $[Fe(n\text{-}C_4H_9C_5H_4)_2]PF_6$: Fe, 12.60; C, 48.78; F, 25.72; H, 5.91. Found: Fe, 12.62; C, 48.86; F, 25.50; H, 5.88.

A sample of **$[Fe(C_5H_5)_2]BF_4$** was prepared by oxidizing ferrocene in $(C_2H_5)_2O$ with *p*-benzoquinone in the presence of HBF_4. A 30-ml $(C_2H_5)_2O$ solution of ferrocene (1 mmol) was mixed with 30 ml of an etherial solution of *p*-benzoquinone (2 mmol) and tetrafluoroboric acid (4 mmol, 50% aqueous solution). The resulting blue precipitate was filtered and washed thoroughly with ether. *Anal.* Calcd for $[Fe(C_5H_5)_2]BF_4$: Fe, 20.47; C, 44.02; F, 27.85; H, 3.69. Found: Fe, 20.64; C, 44.18; F, 27.56; H, 3.92.

$[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Fe]$ and $Fe(C_5H_5)(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})$.—The method of Hawthorne, *et al.*,[12] was used in the preparation of these compounds. Purification was accomplished by three recrystallizations from acetone–water or two from cyclohexane–benzene. *Anal.* Calcd for $[(CH_3)_4N][(DCB)_2Fe]$: Fe, 14.15; B, 49.29; C, 24.34; N, 3.55; H, 8.68. Found: Fe, 14.06; B, 48.74; C, 24.49; N, 3.62; H, 8.58. Calcd for Fe(cp)(DCB): Fe, 22.04; B, 38.40; C, 33.19; H, 6.37. Found: Fe, 22.08; B, 38.27; C, 33.42; H, 6.57.

Magnetic Measurements.—A Princeton Applied Research FM-1 vibrating sample magnetometer, coupled with an Andonian Associates liquid helium dewar, was used in the determinations of the magnetic susceptibilities of solid materials. Temperatures were measured using a copper–constantan thermocouple; the insensitivity of this thermocouple at very low temperatures necessitated the reporting of magnetic susceptibility data only down to 40°K (here the accuracy of a single measurement is *ca.* 10%).

Room-temperature effective magnetic moments (*ca.* 3% accuracy) for solids were measured *vs.* $CuSO_4 \cdot 5H_2O$ standard on the FM-1 magnetometer. These were used to convert the relative machine data resultant from liquid nitrogen runs (300–80°K in 2 hr) and indirectly the relative machine data from liquid helium runs (40–125°K in 1 hr). Duplicate determinations were made for freshly prepared samples of each compound in each range. Time studies of various solids showed no indication of decomposition. Empty-holder diamagnetic corrections were applied throughout the whole temperature range.

The Evans nmr method[13] was used to measure the room-temperature (*i.e.*, the ambient probe temperature was 42°) solution magnetic moments. A Varian A-60 spectrometer was used. Both $Fe(cp)_2^+$ and $Fe(n\text{-}C_4H_9cp)(cp^+)$ were prepared *in situ* by oxidizing the appropriate ferrocene (~3 mmol) with 1 ml of concentrated H_2SO_4 and then diluting to 25 ml with H_2O containing ~2% *tert*-C_4H_9OH. Filtration (and in the case of the butyl-substituted compound extraction with benzene) preceded the nmr measurements. A dilute sulfuric acid solution of $[Fe(cp)_2]BF_4$ was also used to determine the solution effective magnetic moment of the $Fe(cp)_2^+$ ion. In all cases the concentration of the ferricenium ion was measured optically. Density corrections[13] were also applied. Solution stabilities were checked by monitoring the visible spectra; no apparent indication of decomposition was evident for these ferricenium ions over the time period of the susceptibility measurements.

Theory

The $^2E_{2g}(a_{1g})^2(e_{2g})^3$ state of the ferricenium ion is split into two Kramers doublets [E″ and (A′, A″)] under the influence of spin–orbit coupling. Crystal fields of symmetry lower than D_5 mix these two Kramers doublets; wave functions (hole formalism) and energies for the resulting two Kramers doublets have been given,[7] as shown by

$$\psi_\pm{}^a = \begin{cases} N(e_{2g}{}^+ + \zeta e_{2g}{}^-)\alpha \\ N(e_{2g}{}^- + \zeta e_{2g}{}^+)\beta \end{cases} \qquad W(\psi_\pm{}^a) = -(\xi^2 + \delta^2)^{1/2}$$

$$\psi_\pm{}^b = \begin{cases} N(e_{2g}{}^- - \zeta e_{2g}{}^+)\alpha \\ N(e_{2g}{}^+ - \zeta e_{2g}{}^-)\beta \end{cases} \qquad W(\psi_\pm{}^b) = +(\xi^2 + \delta^2)^{1/2}$$

Here the mixing parameter (ζ), spin–orbit coupling constant (ξ), and low-symmetry distortion parameter (δ) are the same as defined previously.[7]

The symmetry of the ferricenium ion will be taken as D_{5d} with the z axis as the fivefold axis. To calculate the parallel ($\chi_{||}$) and perpendicular ($\chi_\perp$) components of the paramagnetic susceptibility we introduce the perturbations $\beta H_z(\hat{L}_z + 2\hat{S}_z)$ and $\beta H_x(\hat{L}_x + 2\hat{S}_x) = \beta H_y \cdot (\hat{L}_y + 2\hat{S}_y)$, respectively. The resulting secular equations are solved for the eigenvalues, which are then used to evaluate the parallel and perpendicular components of the paramagnetic susceptibility of the ferricenium ion by Van Vleck's formula[14]

$$\chi_\alpha = \frac{N\beta^2}{kT\omega_0}\sum_m \left\{ (\langle\psi_{0m}|L_\alpha + 2S_\alpha|\psi_{0m}\rangle)^2 + 2kT\sum_{n\neq 0}\frac{(\langle\psi_n|L_\alpha + 2S_\alpha|\psi_{0m}\rangle)^2}{E_n - E_0}\right\}$$

The α component of the magnetic susceptibility tensor χ_α is evaluated by summing the appropriate expectation values over the m components of the ψ_0 ground state (with degeneracy ω_0) and the n excited states ψ_n.

Considering only the two Kramers doublets from the ferricenium $^2E_{2g}$ ground state, we find for the lower doublet $\psi_\pm{}^a$

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

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

Here the symbols ζ, ξ, and δ are again as defined earlier.[7] Operation with the angular momentum operator has introduced the orbital reduction parameter k'. We have neglected admixtures of states outside the two lowest energy configurations $[(a_{1g})^2(e_{2g})^3$ and $(a_{1g})^1(e_{2g})^4]$ as was done previously.[7] Incorporation of such second-order effects for the ferricenium ion has been found to be minor.[9] The difference in energy, $2(\xi^2 + \delta^2)^{1/2}$, between the lower Kramers doublet $\psi_\pm{}^a$ and the upper doublet $\psi_\pm{}^b$ is too large to have appreciable population in $\psi_\pm{}^b$ even at room temperature.[6,7,9,15] Thus

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[11] T. Pavlik and J. Klikorka, *Collect. Czech. Chem. Commun.*, **30**, 664 (1965).

[12] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

[13] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[14] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

[15] E. D. German and M. E. Dyatkina, *Zh. Strukt. Khim.*, **7**, 866 (1966).

the above susceptibility expressions are appropriate for the ferricenium ion.

The average magnetic susceptibility (χ) and the effective magnetic moments (μ_{eff}) are readily found as

$$\chi = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$$

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

The effective magnetic moment, μ_{eff}, of the ferricenium ion, assuming a $^2E_{2g}$ ground state, would be expected then to be dependent on temperature (see Figure 1), the low-symmetry distortion parameter (δ), and the orbital reduction factor (k'). The mixing parameter, ζ, depends on the ratio of δ and ξ; the latter is given by $\xi = -k'\xi_0$, where ξ_0 is the one-electron spin–orbit coupling constant of a free iron atom.[7] In Figure 1 it can be seen that as the low-symmetry distortion increases, the effective magnetic moment decreases. Even further, the temperature dependence decreases as δ increases; if δ is taken to be very large, as assumed by German and Dyatkina,[9] the effective magnetic moment approaches the spin-only value and is found to be temperature independent. Thus, the magnitude and the temperature dependence of the moment will be useful in characterizing the ground-state manifold of the ferricenium ion.

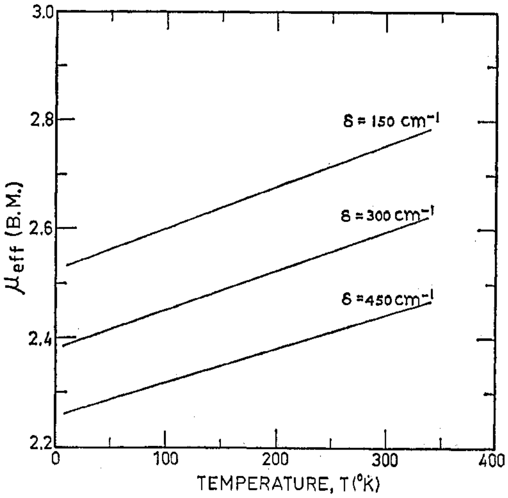

Figure 1.—Theoretical effective magnetic moment (μ_{eff}) *vs.* temperature curves for $\psi_{\pm}{}^{a}({}^2E_{2g})$ ferricenium ground state experiencing different low-symmetry distortions δ. In all cases the orbital reduction parameter $k' = 0.80$.

In anticipation of the Results the above susceptibility expressions for the ferricenium ion will be modified to account for two possibilities. As depicted in Figure 1, μ_{eff} for the ferricenium ion is sensitive to changes in the component of the low-symmetry crystal field which affects the $^2E_{2g}$ manifold, that is, $\delta = \langle e_{2g}{}^{+}|H_{\text{eff}}'|e_{2g}{}^{-}\rangle$. If δ increases with increasing temperature, it is possible to select the temperature functionality of δ such that the μ_{eff} for the ferricenium ion would be essentially temperature independent, while still maintaining a value far in excess of the spin-only value.

Another means of securing a temperature-independent μ_{eff} is the introduction of a low-lying electronic state. Thermal population of the $^2A_{1g}(a_{1g})^1(e_{2g})^4$ state[16] at the higher temperatures would have the desired effect. The magnetic susceptibility expressions then appear as

$$\chi_{\alpha} = \frac{\chi_{\alpha}[\psi_{\pm}{}^{a}({}^2E_{2g})] + e^{-\Delta E/kT}\chi_{\alpha}({}^2A_{1g})}{1 + e^{-\Delta E/kT}}$$

where χ_{α} is either the parallel or perpendicular component of the susceptibility, $\Delta E = \Delta E[{}^2A_{1g} - \psi_{\pm}{}^{a}({}^2E_{2g})]$, and the susceptibilities of the $^2A_{1g}$ state are those of a spin-only state

$$\chi_{\parallel}({}^2A_{1g}) = \chi_{\perp}({}^2A_{1g}) = \frac{N\beta^2}{kT}$$

It should be noted that there are no nonzero matrix elements between the $^2A_{1g}$ and $^2E_{2g}$ states as a result of spin–orbit interaction. If $\Delta E \simeq kT$, thermal population of the $^2A_{1g}$ state will dramatically affect the shape of the μ_{eff} *vs.* T curve at higher temperatures; μ_{eff} can become essentially independent of temperature under these conditions.

As pointed out by Maki and Berry[7] there is a further complication to be considered when the $^2E_{2g}$ and $^2A_{1g}$ states are nearly degenerate. Components of the low-symmetry crystal field will mix the $^2E_{2g}$ and $^2A_{1g}$ states introducing another distortion parameter $\epsilon = \langle e_{2g}{}^{\pm}|\mathcal{H}'|a_{1g}\rangle$. The data at our disposal are not sufficient to include this configuration interaction, but we recognize that our parameter evaluation (δ, k', and ΔE) in the thermal population model is not unique.

Results and Discussion

Room-Temperature Measurements.—Room-temperature magnetic susceptibility measurements were completed for nine ferricenium and two iron(III) dicarbollide (*i.e.*, $B_9C_2H_{11}{}^{2-}$) solid compounds. The requisite ligand and counterion diamagnetic corrections were obtained either from direct measurement or from a table;[17] the results are given in Table I. These diamagnetic corrections were used in the calculations of the room-temperature effective magnetic moments for the compounds listed in Table II. Values obtained previously by other workers are included. Here we also give the 42° nmr solution moments for the $Fe(cp)_2{}^+$ and $Fe(n\text{-}C_4H_9cp)(cp)^+$ ions in dilute sulfuric acid.

The room-temperature moments of the low-spin d^5 iron in these ferricenium and dicarbollide complexes range from ~2.3 to ~2.6 BM. This degree of devia-

TABLE I

VARIOUS DIAMAGNETIC CORRECTIONS USED IN THE TREATMENT OF EXPERIMENTAL DATA

Species	Diamagnetism (×10⁶), cgsu	Species	Diamagnetism (×10⁶), cgsu
$PF_6{}^-$	−23.0[a]	$I_4{}^-$	−184.1[b]
$BF_4{}^-$	−122.0[a]	$Fe(cp)_2$	−125.0[c]
pic⁻	−147.6[a]	$Fe(n\text{-}C_4H_9cp)(cp)$	−172.4[d]
$Co(DCB)_2{}^-$	−257.1[a,e]	$Fe(n\text{-}C_4H_9cp)_2$	−219.8[d]
$(CH_3)_4N^+$	−60.3[a]	$Fe(C_6H_5cp)(cp)$	−172.7[d]
$I_3{}^-$	−139.5[a]		

[a] Determined by direct measurement of appropriate compound. [b] Taken as $\chi_M(I_3{}^-) + {}^1/_2\chi_M(I_2)$, the latter value from tables.[17] [c] F. Englemann, *Z. Naturforsch. B*, **8**, 775 (1953). [d] Taken as χ_M(ferrocene) + χ_M(substituent), the latter value from tables.[17] [e] This value is used as a diamagnetic correction for the $Fe(DCB)_2{}^-$ calculation.

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[16] The proximity of the $^2E_{2g}$ and $^2A_{1g}$ states in the ferricenium ion has been alluded to briefly in ref 5a; further details will follow in another paper.

[17] J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960.

TABLE II

ROOM-TEMPERATURE EFFECTIVE MAGNETIC MOMENTS FOR VARIOUS FERRICENIUM AND ANALOGOUS COMPOUNDS

Compd[a]	μ_{eff}(298°K), BM
$[Fe(cp)_2]PF_6$	2.62
$[Fe(cp)_2]pic$	2.60, 2.26[b]
$[Fe(cp)_2]I_3$	2.47, 2.34 ± 0.12[c]
$[Fe(cp)_2]BF_4$	2.44, 2.49[d]
$[Fe(cp)_2]ClO_4$	2.34[e]
$[Fe(n\text{-}C_4H_9cp)(cp)]PF_6$	2.54
$[Fe(n\text{-}C_4H_9cp)(cp)]pic$	2.48
$[Fe(n\text{-}C_4H_9cp)(cp)]I_3$	2.53
$[Fe(n\text{-}C_4H_9cp)_2]PF_6$	2.59
$[Fe(C_6H_5cp)(cp)]I_4$	2.58
$(CH_3)_4NFe(DCB)_2$	2.58
$Fe(DCB)_2^-$(soln)[f]	2.10[g]
$Fe(DCB)(cp)$[f]	2.23
$[(CH_3)_4N]\{Fe[1,2\text{-}B_9H_9C_2(CH_3)_2]_2\}$	2.45[e]
$Fe[1,2\text{-}B_9H_9C_2(CH_3)_2]_2^-$(soln)	1.99[g]
$Fe(cp)_2^+$(soln)	2.31[h]
$[Fe(cp)_2]BF_4$(soln)	2.48[h]
$Fe(n\text{-}C_4H_9cp)(cp)^+$(soln)	2.38[h]

[a] All compounds are solids unless otherwise stated. [b] G. Wilkinson, M. Rosenblum, M. Whiting, and R. B. Woodward, *J. Amer. Chem. Soc.*, **74,** 2125 (1952). [c] F. Englemann, *Z. Naturforsch. B*, **8,** 775 (1953). [d] G. Stolzle, Dissertation, University of Munich, 1961. [e] J. S. Little, P. S. Welcker, N. J. Soy, and S. J. Todd, *Inorg. Chem.*, **9,** 63 (1970). [f] DCB ≡ $1,2\text{-}B_9C_2H_{11}^{2-}$. [g] From ref 12; magnetic moments measured in acetone solution. [h] Measured in dilute H_2SO_4 by Evans' nmr method,[13] at an ambient probe temperature of 42°.

tion from the spin-only value of 1.73 BM establishes the $^2E_{2g}$ ground state for the ferricenium ion, in agreement with two esr studies,[6,7] and shows that the low-symmetry distortion (or Jahn–Teller) is not as large as was assumed by German and Dyatkina.[9] If the distortion were so large, the orbital contribution to the magnetic moment would be quenched leaving an essentially spin-only value for μ_{eff}. Sufficient precautions were taken to rule out the alternative possibility of a $^2A_{1g}$ ground state with paramagnetic impurities.

The solution moments measured for the two different ferricenium ions are relatively low. In the case of two iron dicarbollide complexes both solid and solution moments are known and the latter are appreciably smaller. These data suggest that in solution the ferricenium ion is much more significantly distorted than it is in the solid (see Figure 1).

Some evidence for solvent interaction with ferricenium complexes was found in the nmr experimentation. In our application of the nmr method for solution magnetic moments *tert*-C_4H_9OH (2% in H_2O) was used as the monitor of the bulk susceptibility of the solution. We have found that for aqueous solutions of $Fe(cp)_2^+$ and $Fe(n\text{-}C_4H_9cp)(cp)^+$ the shift in the water peak greatly exceeded (~70%) that observed in the *tert*-C_4H_9OH peak. Close radial (*i.e.*, *xy* plane) approach would result in a pseudocontact interaction causing a larger peak shift for the water protons. Thus there is clear indication of a specific interaction of water with the ferricenium ion. Our conclusion is further supported by evidence which shows that the aqueous ferricenium ion is bound by certain carboxylic acids.[18] It appears that in solution the ferricenium ion is coordinated to a solvent molecule and that this coordination results in a distortion greater than that experienced in the solids. Any consideration of the temperature dependence of the solution μ_{eff} or other magnetic property (*e.g.*, pseudocontact nmr shift) of the ferricenium ion would require a careful evaluation of this effect.

Variable-Temperature Measurements.—Variable-temperature magnetic susceptibility studies in the range of 40–300°K resulted in the μ_{eff} *vs.* T curves depicted in Figures 2–5. In the case of four compounds, data were only collected down to 80°K. It is clear from these figures, however, that all 11 μ_{eff} *vs.* T curves have essentially the same shape. Ring substitution and counterion interchange have the effect only of displacing the curve for a particular compound to higher or lower effective magnetic moment. Thus monobutylation leads to a ~0.1-BM change for the hexafluorophosphates (see Figure 3), whereas, 1,1′-dibutylation leaves the moment essentially unchanged. It seems that the more asymmetric the ion as a result of substitution, the more pronounced is the change in μ_{eff}. Monobutylation in the picrate and triiodide series (see Figures 3 and 4) gives the same order of change in μ_{eff} as observed for the hexafluorophosphates. Unfortunately, we were not able to prepare the disubstituted ferricenium picrate and triiodide compounds. Total interchange of the dicarbollide ion for the cyclopentadienide ion results in no dramatic change (compare the position of the curve

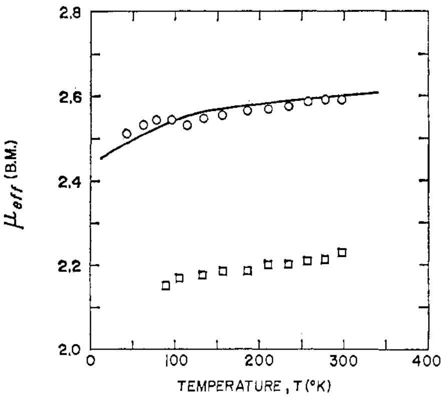

Figure 2.—Curves of the effective magnetic moment (μ_{eff}) *vs.* temperature for two iron(III) dicarbollide (*i.e.*, $1,2\text{-}B_9C_2H_{11}^{2-}$ ≡ DCB^{2-}) compounds: ○, $[(CH_3)_4N][Fe(DCB)_2]$; □, Fe(cp)(DCB). The solid line is a theoretical curve for the thermal population model with δ = 240 cm^{-1} and ΔE $[E'(^2A_{1g}) - \psi_\pm{}^a(^2E_{2g})]$ = 520 cm^{-1}.

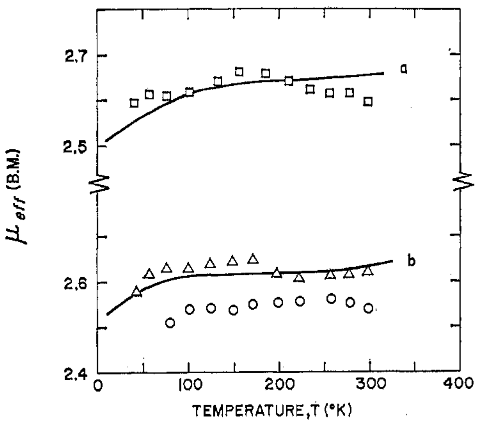

Figure 3.—Curves of the effective magnetic moment (μ_{eff}) *vs.* temperature for three different ferricenium hexafluorophosphates: □, $[Fe(n\text{-}C_4H_9C_5H_4)_2]PF_6$; Δ, $[Fe(C_5H_5)_2]PF_6$; ○, $[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)]PF_6$. The solid lines are theoretical curves for the thermal population model: a, δ = 180 cm^{-1}, ΔE = 540 cm^{-1}; b, δ = 160 cm^{-1}, ΔE = 400 cm^{-1}.

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for the bis-dicarbollide compound in Figure 2 with those for various unsubstituted ferricenium salts in Figures 3–5). Replacement of one of the cyclopentadienyl ligands by dicarbollide, giving the nonionic compound $Fe(cp)(1,2\text{-}B_9C_2H_{11})$, results in a low magnetic moment (see Figure 2). Since this is the only nonionic d^5 ferricenium-like complex considered, it is reasonable to suggest that the low moment is due to a distortion caused by packing the asymmetric molecule into the crystal.

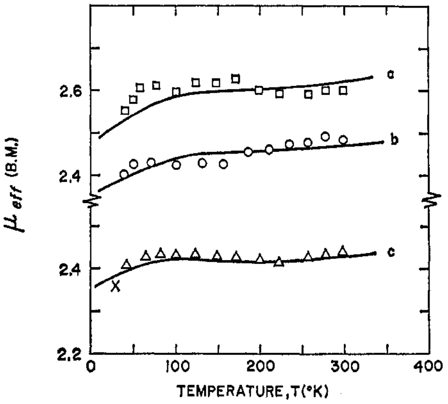

Figure 4.—Curves of the effective magnetic moment (μ_{eff}) *vs.* temperature for three ferricenium salts: □, $[Fe(C_5H_5)_2]pic$; ○, $[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)]pic$; △, $[Fe(C_5H_5)_2]BF_4$. The solid lines are theoretical curves for the thermal population model: a, $\delta = 200$ cm^{-1}, $\Delta E = 460$ cm^{-1}; b, $\delta = 330$ cm^{-1}, $\Delta E = 400$ cm^{-1}; c, $\delta = 330$ cm^{-1}, $\Delta E = 380$ cm^{-1}. The X represents the μ_{eff} obtained by esr in ref 6 for frozen DMF and acetone solutions of $[Fe(C_5H_5)_2]BF_4$.

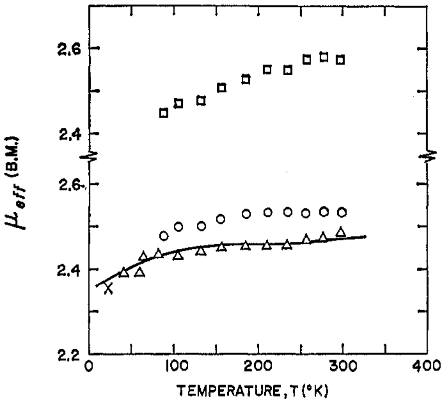

Figure 5.—Curves of the effective magnetic moment (μ_{eff}) *vs.* temperature for three ferricenium salts: □, $[Fe(n\text{-}C_4H_9C_5H_4)(C_5H_5)]I_3$; ○, $[Fe(C_5H_5)_2]I_3$; △, $[Fe(C_6H_5C_5H_4)(C_5H_5)]I_4$. The solid line is a theoretical curve for the thermal population model with $\delta = 330$ cm^{-1} and $\Delta E = 400$ cm^{-1}. The X represents the μ_{eff} obtained by esr in ref 6 for frozen DMF and acetone solutions of $[Fe(C_5H_5)_2]I_3$.

The solution moment (Table II) determined for the ferricenium ion is essentially that found for either $[Fe(cp)_2]BF_4(s)$ or $[Fe(cp)_2]I_3(s)$. It appears that the distortion felt by the ferricenium ion in solution is the same as that in the triiodide and tetrafluoroborate solids. Prins and Reinders[3] measured the esr spectra for these same two solids in frozen solutions of dimethylformamide and acetone at 20°K. Their g values give $\mu_{eff} = 2.36$ BM at 20°K for the ferricenium ion; it is thus not surprising that this μ_{eff} value fits on our μ_{eff} *vs.* T curves for both $[Fe(cp)_2]BF_4(s)$ and $[Fe(cp)_2]I_3(s)$ (see Figures 4 and 5).

From Figures 1–5 it can be seen that we are dealing with ferricenium ions or iron(III) dicarbollide ions which are seemingly experiencing low-symmetry crystal field distortions ($\delta = \langle e_{2g}^{+}|H_{eff}'|e_{2g}^{-}\rangle$) in the range of ~200–300 cm^{-1}. Distortions of this magnitude would be difficult to detect in an X-ray structure determination. X-Ray structure determinations have been reported for two ferricenium salts, $[Fe(cp)_2]I_3$[19] and $[Fe(cp)_2]pic$.[20] In both cases it was not even possible to give a good description of the cyclopentadienide ring conformations. Some evidence for distortion of the ferricenium ion has been obtained, however, in an infrared study of a series of ferricenium salts.[21]

A comparison of the experimental μ_{eff} *vs.* T data (Figures 2–5) with the theoretical curves (Figure 1) generated for the $^2E_{2g}$ ground state ferricenium ion experiencing a temperature-independent, low-symmetry distortion (δ) is instructive. Theoretically μ_{eff} should increase with increasing temperature, but experimentally μ_{eff} is found to be relatively temperature independent. In the Theory two different modifications of the theoretical susceptibility expression were proposed to give a temperature-independent μ_{eff}. Perhaps the simplest approach would be to take δ as temperature dependent. From Figure 1 we can see that if δ increases with increasing temperature the experimental curves can be fit. Thus as the crystal expands with increasing temperature, the low-symmetry distortion increases, possibly due to increased motion of the cyclopentadienyl rings.

The second modification of the susceptibility expression given in the Theory involves consideration of the low-lying $^2A_{1g}$ state.[16] If this state becomes thermally populated as the temperature increases, a temperature-independent μ_{eff} could result. Assuming $\epsilon = 0$ (see Theory), theoretical curves (see Figures 2–5) have been visually fit to the experimental data for seven of the compounds. We have elected to assume the same orbital reduction parameter ($k' = 0.80$) in each case. Within the framework of this thermal population model the distortion parameter δ for these seven compounds varies from ~160 to ~330 cm^{-1}, whereas $\Delta E[^2A_{1g} - \psi_{\pm}{}^{a}(^2E_{2g})]$ varies from ~380 to ~540 cm^{-1}. The variation in δ is well outside the range of experimental uncertainties; the distortion seems to reflect changes in the anion environment mainly, where small anions and water solvent molecules cause the larger distortions. Thus changing the anion from PF_6^- to the relatively small BF_4^- results in a difference of ~0.2 BM in μ_{eff} for the unsubstituted ferricenium ion.

In summary, it is clear that the experimental magnetic susceptibility curves obtained for various ferricenium compounds cannot be explained by considering only the two Kramers doublets from the $^2E_{2g}$ ground state with a temperature-independent distortion δ. It is necessary to introduce $\delta(T)$ or thermal population of the $^2A_{1g}$ state to explain the relative temperature independence of μ_{eff}. We are undertaking spectroscopic studies and single-crystal susceptibility measurements in an attempt to distinguish between these possibilities.

Acknowledgments.—This research was supported by the National Science Foundation.

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