Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, Canada, V6T 1W5

${}^5T_{2g}$–${}^1A_{1g}$ Spin Crossover in Tris[2-(2′-pyridyl)benzimidazole]iron(II) Complexes

JOHN R. SAMS* and TSANG BIK TSIN

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Seven new octahedral ferrous complexes of 2-(2′-pyridyl)benzimidazole (pyben) have been prepared and characterized by Mössbauer, ir, and visible spectra and conductance and magnetic susceptibility measurements. Six of the complexes are of the type $Fe(pyben)_3A_2 \cdot xH_2O$ [A = I, NCS, BF_4, $B(C_6H_5)_4$, $Cr(NH_3)_2(NCS)_4$; x = 0, 1, 2, but not all combinations]. These salts all show temperature-dependent ${}^5T_{2g}$–${}^1A_{1g}$ spin crossover between 4.2 and 295 K. Details of the spin crossover are sensitive to the nature of the anion and the number of waters of crystallization. The asymmetric nature of the ligand allows in principle the occurrence of vicinal and meridional geometrical isomers of the $Fe(pyben)_3{}^{2+}$ cation. Only the meridional isomer is found to occur in these derivatives. The covalent complex $Fe(pyben)_2(NCS)_2$ is fully high-spin down to 4.2 K. The molecule is tetragonally distorted and has an $|xy\rangle$ orbital singlet ground state.

Introduction

We have recently reported studies on four iron(II) complexes of the bidentate chelating ligand 2-(2′-pyridyl)benzimidazole (pyben), namely, $Fe(pyben)_3Br_2$, $Fe(pyben)_3(NO_3)_2 \cdot H_2O$, and $Fe(pyben)_3(ClO_4)_2 \cdot xH_2O$ (x = 1, 2).[1,2] All four compounds showed anomalous magnetic behavior, and Mössbauer data clearly established that in each case there was a temperature-dependent spin crossover between ${}^5T_{2g}$ and ${}^1A_{1g}$ ground terms. From solution and solid-state electronic spectra it was also shown[2] that the ground-state spin crossover phenomenon in these complexes was exclusively a solid-state effect.

Our results also raised two interesting questions. First, details of the ${}^5T_{2g}$–${}^1A_{1g}$ crossover were clearly dependent on the anion present, but the range of anions studied was not sufficiently broad to establish any obvious trends. Second, for the perchlorate complexes both magnetic moments and Mössbauer area fractions were quite different for x = 1 and 2. The second water of crystallization in the dihydrate is very weakly held and can be removed on the vacuum line at room temperature. A similar although less pronounced effect of the hydration state on magnetic properties had been observed for $Fe(pyim)_3SO_4 \cdot xH_2O$ (x = 2, 3; pyim = 2-(2′-pyridyl)imidazole)[3a] but had not been commented upon. Sylva and Goodwin[3b] also reported that the hydration state of salts containing the bis[2-(2-pyridylamino)-4-(2-pyridyl)thiazole]iron(II) ion could in some instances influence the magnetism. It was of interest to see if this phenomenon would be observed in other cases as well. In an attempt to clarify these questions we have now prepared and characterized seven additional ferrous complexes of pyben and report our results here.

Experimental Section

Magnetic susceptibilities, molar conductances, and infrared and electronic spectra were obtained by methods described in ref 2. Molar conductances (ca. 10^{-3} M solutions in methanol) at 25 °C are given in Ω^{-1} cm^2 mol^{-1}. Wavelengths of maximum absorption in the electronic spectra (methanol solutions at 25 °C) are given in nm with molar extinction coefficients in parentheses. Iron analyses were carried out with a Perkin-Elmer 305A atomic absorption spectrophotometer. Other analyses were performed either by Mr. P. Borda of this department or by Drs. F. Pascher and E. Pascher, Mikroanalytical Laboratorium, Bonn, Germany.

The Mössbauer spectrometers and the cryostats employed for variable-temperature and magnetic perturbation Mössbauer measurements have been described previously.[1,4-6] Calibration of the Doppler velocity scale was affected with an iron-foil absorber, and isomer shifts are given relative to the centroid of the disodium pentacyanonitrosylferrate(II) spectrum. For spectra obtained in the absence of an applied magnetic field, the data points were fitted by least-squares techniques to Lorentzian components. In most cases no constraints were imposed on the fitting parameters. However, for some of the spectra which consisted of two strong and two weak absorptions, we could not fit the weak lines with unconstrained parameters. In these cases the widths of the two weak lines were constrained to be equal in order to achieve a four-line fit. The two line widths were then varied in steps of 0.01 mm s^{-1} in each direction (although still constrained to be equal) until a minimum in the standard deviation of the fit was obtained. This was then accepted as the preferred solution. Theoretical magnetic perturbation Mössbauer spectra were computed by Lang's program.[7] Determinations of the sign of the electric field gradient and magnitude of the asymmetry parameter were by visual inspection as described elsewhere.[8]

All chemicals were obtained from commercial sources and used without further purification. The initial stages of all of the preparations of the complexes were carried out in a dry nitrogen atmosphere, owing to the air sensitivity of the ferrous starting materials.

Tris[2-(2′-pyridyl)benzimidazole]iron(II) Iodide, $Fe(pyben)_3I_2$. A solution of anhydrous ferrous chloride (0.2 g, 1.6 mmol) in methanol (30 ml) was added to a solution of 2-(2′-pyridyl)benzimidazole (1.1 g, 5.6 mmol) in methanol (80 ml). The resulting deep red solution was filtered through a fine sintered-glass filter into 50 ml of an aqueous solution containing 5.0 g (30.6 mmol) of potassium iodide. The solution was concentrated to ca. 80 ml under reduced pressure and cooled in an ice bath for 4 h. The deep orange crystals which formed were collected by filtration, washed several times with cold water, and dried in vacuo. Anal. Calcd for $C_{36}H_{27}N_9FeI_2$: C, 48.30; H, 3.04; N, 14.08; Fe, 6.24. Found: C, 47.97; H, 3.00; N, 14.00; Fe, 6.23. Λ_M = 169 Ω^{-1} cm^2 mol^{-1}; λ 490 nm (9.8×10^2).

Tris[2-(2′-pyridyl)benzimidazole]iron(II) Thiocyanate Monohydrate, $Fe(pyben)_3(NCS)_2 \cdot H_2O$. 2-(2′-Pyridyl)benzimidazole (1.2 g, 6.1 mmol) was dissolved in 70 ml of 95% ethanol and 55 ml of water was added. Ferrous ammonium sulfate (0.7 g, 1.8 mmol) was dissolved in water (70 ml) to which was added 50 ml of 95% ethanol. The ice-cold ferrous ammonium sulfate solution was added with stirring to the ligand solution in an ice bath, and potassium thiocyanate (1.6 g, 16 mmol) dissolved in ice-cold water (30 ml) was immediately added. The resulting red solution was left in the ice bath overnight. The large orange crystals were filtered off, washed with cold water several times, and dried in vacuo. Anal. Calcd for $C_{38}H_{29}N_{11}FeS_2O$: C, 58.84; H, 3.77; N, 19.86; Fe, 7.20. Found: C, 58.55; H, 3.86; N, 19.88; Fe, 7.20. The complex is unstable in methanol solution.

Dithiocyanatobis[2-(2′-pyridyl)benzimidazole]iron(II), $Fe(pyben)_2(NCS)_2$. Anhydrous ferrous chloride (0.5 g, 3.9 mmol) in methanol (50 ml) was added to a solution of the ligand (2.3 g, 11.8 mmol) in methanol (100 ml). The deep red solution was added to a large excess of potassium thiocyanate (5.0 g, 51 mmol) dissolved in a minimum volume of water, and the solution was boiled under reflux for 15 min. The red precipitate which formed was collected, recrystallized from methanol, and dried in vacuo. Anal. Calcd for $C_{26}H_{18}N_8FeS_2$: C, 55.52; H, 3.23; N, 19.92; Fe, 9.93. Found: C, 55.59; H, 3.38; N, 19.74; Fe, 9.88. Λ_M = 79 Ω^{-1} cm^2 mol^{-1}; λ 474 nm (5.7×10^2).

Tris[2-(2′-pyridyl)benzimidazole]iron(II) Tetrafluoroborate Monohydrate, $Fe(pyben)_3(BF_4)_2 \cdot H_2O$. $Fe(pyben)_3Br_2$ (1.3 g, 1.6 mmol) prepared as in ref 2 was dissolved in methanol (230 ml) and added to 150 ml of an aqueous solution containing 4.0 g (38 mmol) of ammonium tetrafluoroborate. The red solution was concentrated to 180-ml volume. The crystals which formed were collected on a filter and washed several times with water to remove excess NH_4BF_4. The crude compound was recrystallized by dissolving it in methanol (150 ml) and concentrating the solution to about 30-ml volume; precipitation was then effected by the addition of water (5 ml). The purple crystals were collected and washed with water. The monohydrate was obtained as an orange product after the purple crystals were dried in vacuo. Anal. Calcd for $C_{36}H_{29}N_9FeB_2F_8O$: C, 51.89; H, 3.51; N, 15.13. Found: C, 52.14; H, 3.37; N, 15.42. $\Lambda_M = 177\ \Omega^{-1}\ cm^2\ mol^{-1}$; λ 490 nm (10.2×10^2).

Tris[2-(2′-pyridyl)benzimidazole]iron(II) Tetrafluoroborate Dihydrate, $Fe(pyben)_3(BF_4)_2{\cdot}2H_2O$. The procedure was identical with that used for the monohydrate derivative above, except that the purple crystals were dried in air to give a stable brown compound. Anal. Calcd for $C_{36}H_{31}N_9FeB_2F_8O_2$: C, 50.80; H, 3.67; N, 14.81. Found: C, 50.51; H, 3.40; N, 14.61. $\Lambda_M = 192\ \Omega\ cm^2\ mol^{-1}$; λ 490 nm (9.8×10^2).

Tris[2-(2′-pyridyl)benzimidazole]iron(II) Tetraphenylborate Monohydrate, $Fe(pyben)_3(BPh_4)_2{\cdot}H_2O$. $Fe(pyben)_3Br_2$[2] (1.0 g, 1.2 mmol) dissolved in 95% ethanol (400 ml) was added to a solution of sodium tetraphenylborate (2.0 g, 5.8 mmol) in 95% ethanol (150 ml). The solution was concentrated to a volume of 175 ml and left to stand overnight at 0 °C. The red precipitate which formed was filtered off and dried in vacuo. Anal. Calcd for $C_{84}H_{69}N_9FeB_2O$: C, 77.73; H, 5.36; N, 9.71. Found: C, 77.86; H, 4.95; N, 9.68. The complex was not sufficiently soluble for conductance and spectral measurements.

Tris[2-(2′-pyridyl)benzimidazole]iron(II) Tetrathiocyanatodiamminechromate(III), $Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$. A solution of $Fe(pyben)_3Br_2$[2] (1.1 g, 1.4 mmol) in methanol (175 ml) was added to a solution of Reinecke salt (1.0 g, 2.8 mmol) in methanol (160 ml). Water (20 ml) was added and the volume of the solution reduced to about 100 ml. The precipitate which formed was collected by filtration, washed with a 1:1 methanol–water mixture, and dried in vacuo. Anal. Calcd for $C_{44}H_{39}N_{21}FeCr_2S_8$: C, 41.32; H, 3.08; N, 23.02. Found: C, 41.41; H, 3.02; N, 22.68. The complex was not sufficiently soluble for conductance and spectral measurements.

Results and Discussion

The tris[2-(2′-pyridyl)benzimidazole]iron(II) complexes are stable with respect to oxidation, although $Fe(pyben)_3(BF_4)_2{\cdot}H_2O$ and the previously reported[2] $Fe(pyben)_3(ClO_4)_2{\cdot}H_2O$ are converted to their respective dihydrates on exposure to atmospheric moisture. Both dihydrates can be restored to the monohydrate form by pumping the samples at room temperature, although the remaining water of crystallization cannot be removed in vacuo at temperatures up to 150 °C.

In the case of the thiocyanate anion a second type of compound, $Fe(pyben)_2(NCS)_2$, is also formed in which the anion is coordinated directly to the central metal ion. The formation of $Fe(pyben)_3(NCS)_2{\cdot}H_2O$ can be effected by keeping the reaction temperature at 0 °C and using excess ligand in a mixed water–methanol solvent. However, $Fe(pyben)_2(NCS)_2$ appears to be by far the more stable of the two complexes and can be prepared either by boiling the $(pyben)_3$ compound in methanol or, directly at room temperature, by using a ligand:metal mole ratio of 2:1 in a methanolic solution. Even at room temperature $Fe(pyben)_3(NCS)_2{\cdot}H_2O$ decomposes fairly quickly in methanol, losing 1 mol of ligand to form $Fe(pyben)_2(NCS)_2$ (observed by ir and electronic spectra, conductance measurements, and microanalysis of the final product). The behavior of the thiocyanate derivatives is quite unique in this series of complexes, since the other salts appear to be stable in solution for periods of up to several weeks.

Several attempts were made to prepare a chloride salt, since a compound of the formula $Fe(pyben)_3Cl_2{\cdot}6H_2O$ was reported by Chiswell et al.[9] However, all efforts to obtain this hexahydrate by published[9] and other procedures were unsuccessful in our hands, although we did obtain an impure salt thought to be $Fe(pyben)_3Cl_2$ contaminated with free ligand (no band due to H_2O was found in the ir spectrum). The problem here is that the chloride salt is quite soluble in both methanol and water, so that the precipitation procedure used for the other salts is ineffective in this case. When the water:methanol ratio is raised sufficiently to bring down the salt, free ligand coprecipitates. Attempts to isolate the chloride from acetone–water and ethanol–water mixtures were equally unsuccessful.

Efforts to prepare salts of the type $Fe(pyben)_3B$, where B is a dinegative ion, yielded very intractable products for $B^{2-} = CO_3^{2-}$, SO_4^{2-}, and $S_2O_3^{2-}$ and were not pursued further.

The molar conductances of $\sim 10^{-3}$ M solutions of the $Fe(pyben)_3^{2+}$ complexes in methanol at 25 °C are all quite similar and lie in the expected range[10] for 2:1 electrolytes in this solvent. $Fe(pyben)_2(NCS)_2$ shows a much lower conductance, and its Λ_M value is barely in the range expected for a 1:1 electrolyte (80–115 $\Omega^{-1}\ mol^{-1}\ cm^2$ for 10^{-3} M solutions in methanol).[10] This may indicate solvolysis of the covalent complex into species such as $[Fe(pyben)_2(CH_3OH)(NCS)]^+$ and $[Fe(pyben)_2(CH_3OH)_2]^{2+}$.[11]

With the exception of $Fe(pyben)_2(NCS)_2$, all of the complexes have very similar molar extinction coefficients and wavelengths of maximum absorption at 25 °C in methanol solutions. The intensity of the 490-nm band in these complexes is abnormally high for a d–d transition but an order of magnitude lower than usually observed for a $t_{2g} \rightarrow \pi^*$ charge-transfer transition. We think it more likely that this band corresponds to the ${}^5T_{2g} \rightarrow {}^5E_g$ d–d transition and that its unusual intensity may be due to "intensity stealing" from the strong ligand absorption at 330 nm ($\epsilon_{max} \simeq 1.2 \times 10^4$).[2] This assignment yields a crystal field splitting $10Dq \simeq 20\,000$ cm^{-1}, which is in the range expected[12] for a d^6 ferrous system near the ${}^5T_{2g}$–${}^1A_{1g}$ crossover point.

Infrared Data. Infrared spectra between 4000 and 250 cm^{-1} were obtained for all of the complexes. Due to the large number of ligand bands present the spectra are very complex, but the bands which can be assigned to the cation $Fe(pyben)_3^{2+}$ are quite similar to those reported[2,13] for similar transition metal complexes of this ligand and indicate that both the pyridine and imidazole nitrogens are involved in coordination to the central metal ion. We shall therefore confine our attention to the anion modes and the absorptions due to waters of crystallization.

The lattice water in $Fe(pyben)_3(NCS)_2{\cdot}H_2O$ absorbs at 3350 cm^{-1} and this H_2O molecule cannot be removed by pumping the sample at 150 °C. The CN stretch (ν_1) of the NCS^- anion occurs at a slightly lower frequency (2030 cm^{-1}) than in potassium thiocyanate (2050 cm^{-1}), but the line remains unsplit. The ν_2 band appears as a weak absorption at exactly the same position as in KNCS (471 cm^{-1}) while ν_3 is not observed, probably masked by a strong ligand band at 744 cm^{-1}.

There is no appreciable difference between the spectrum of $Fe(pyben)_2(NCS)_2$ and that of $Fe(pyben)_3(NCS)_2{\cdot}H_2O$ as far as ligand bands are concerned. However, $Fe(pyben)_2(NCS)_2$ does not have a lattice water band in the region above 3000 cm^{-1}, and the thiocyanate CN stretch appears as a strong doublet at 2080 and 2022 cm^{-1}. The reported splitting of this band is only about 10 cm^{-1} in the analogous $Fe(phen)_2(NCS)_2$ and $Fe(bpy)_2(NCS)_2$ complexes[13,14] (phen = 1,10-phenanthroline, bpy = 2,2′-bipyridyl). If we assume that in all three cases a cis-octahedral configuration is adopted, the larger splitting here (58 cm^{-1}) may be due to the fact that the pyben ligand is asymmetric while phen and bpy are symmetric ligands. The N–C–S bending mode (ν_2) is found at 474 cm^{-1} as a weak band. Further evidence that the thiocyanate group is coordinated to iron in $Fe(pyben)_2(NCS)_2$ is the appearance of a strong 788-cm^{-1} band which can be assigned[15] to the C–S stretch (ν_3) of the NCS ligand. The position of this band is indicative of N-bonded thiocyanate ligands.[15]

For the pair $Fe(pyben)_3(BF_4)_2{\cdot}H_2O$ and $Fe(pyben)_3(BF_4)_2{\cdot}2H_2O$, the spectra are identical except that there is one

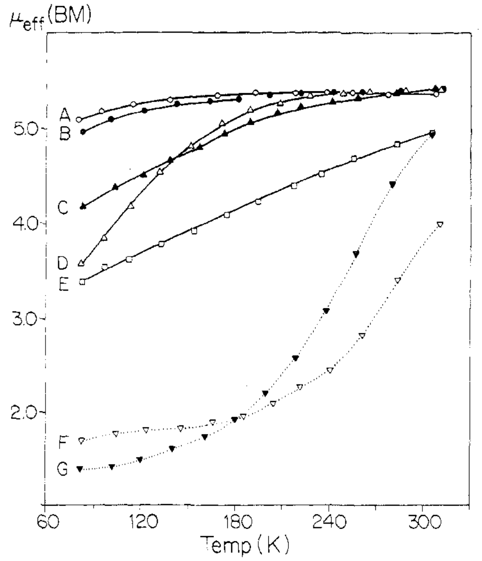

Figure 1. Temperature dependence of the effective magnetic moments μ_{eff} of the complexes: A, $Fe(pyben)_2(NCS)_2$; B, $Fe(pyben)_3(NCS)_2{\cdot}H_2O$; C, $Fe(pyben)_3(BF_4)_2{\cdot}H_2O$; D, $Fe(pyben)_3I_2$; E, $Fe(pyben)_3(BPh_4)_2{\cdot}H_2O$; F, $Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$; G, $Fe(pyben)_3(BF_4)_2{\cdot}2H_2O$.

broad band at 3278 cm^{-1} for the monohydrate while the dihydrate has an extra band with a double maximum at 3528 and 3598 cm^{-1}. The latter can be eliminated by pumping the dihydrate at room temperature. The BF_4^- bands appear at the expected positions:[16] ν_3 at 1053 cm^{-1} is strong and broad, ν_4 is found at 518 cm^{-1} with a splitting of less than 5 cm^{-1} (due presumably to crystal effects), and ν_1 appears as a strong band at 759 cm^{-1}.

The spectral bands due to the $Cr(NH_3)_2(NCS)_4^-$ ion in $Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$ are similar to those of other reineckates,[17] indicating a similar anion environment. The CN stretch appears at 2063 cm^{-1}, and the NCS bending mode occurs at 494 cm^{-1}. The $Cr-NH_3$ stretch appears at 466 cm^{-1} as a weak shoulder. The NH_3 deformation absorptions are at the same positions as in ammonium reineckate:[14] the symmetric deformation at 1257 cm^{-1} and the rocking mode at 708 cm^{-1}. A strong band at 350 cm^{-1} can be assigned to the Cr–NCS stretch while the C–S stretch appears at 848 cm^{-1}.

The lattice water absorption in $Fe(pyben)_3(BPh_4)_2{\cdot}H_2O$ produces a broad band at 3304 cm^{-1}. The infrared spectrum due to the BPh_4^- anion is very complicated and a complete analysis could not be found in the literature. Comparison of the band due to the BPh_4^- ion in the complex with the spectrum of $NaBPh_4$ in the range 2000–250 cm^{-1} revealed that both the positions and intensities of the bands are similar in the two compounds. This suggests a similarity of anion environment. The strongest bands are due to phenyl C–H out-of-plane deformations[18] and appear at 741 and 714 cm^{-1} with intensities similar to the corresponding bands in $NaBPh_4$.

Magnetic Data. The temperature dependence of the effective magnetic moment μ_{eff} varies markedly from compound to compound, and the complexes can be separated very roughly into four groups (see Figure 1). The two thiocyanate derivatives have μ_{eff} values between about 5.0 and 5.4 μ_B throughout the temperature range 78–310 K. The iodide and tetrafluoroborate monohydrate complexes have moments of ~5.4 μ_B at room temperature, decreasing to 3.6–4.2 μ_B at liquid nitrogen temperature. For the tetraphenylborate derivative the moment decreases almost linearly from 5.0 to 3.4 μ_B between 300 and 80 K. The μ_{eff} values for the tetrafluoroborate dihydrate and reineckate salts have the most pronounced temperature dependence, being $\lesssim 1.7$ μ_B at 80 K and being in the range 4.0–5.0 μ_B at room temperature.

All susceptibility measurements were made at two different field strengths, and in no case was a field dependence observed. Moreover, the data were recorded with both descending and ascending temperature and there was no evidence of thermal hysteresis.

Typical high-spin ferrous complexes have moments of about 5.4 μ_B with only a very slight temperature dependence between 80 and 300 K.[6] Thus, with the exception of the thiocyanates, all of the present complexes show anomalous magnetic properties. Mössbauer spectra (vide infra) indicate that these anomalies result from $^5T_{2g}-^1A_{1g}$ crossover, and it is convenient to discuss the magnetic data in terms of this change in spin state.

Although the μ_{eff} values for both $Fe(pyben)_3(NCS)_2{\cdot}H_2O$ and $Fe(pyben)_2(NCS)_2$ have slight temperature dependence and are nearly identical throughout the accessible temperature range, Mössbauer data indicate that the former complex exhibits $^5T_{2g}-^1A_{1g}$ crossover below ~170 K whereas the latter shows no $^1A_{1g}$ component even at 4.2 K. It is clear from these examples that the magnetic data do not guarantee the purity of the spin state. Since the use of μ_{eff} values to extract such parameters as crystal field splittings, spin–orbit coupling constants, and orbital reduction factors[6,12] is not valid if a compound exists as a mixture of spin states, it is essential in such cases to have other evidence (such as Mössbauer spectra) to ensure that only one spin state is present before analyzing μ_{eff} values theoretically.

The μ_{eff} vs. T curve for $Fe(pyben)_3I_2$ is almost identical with that found previously for $Fe(pyben)_3Br_2$.[1,2] This suggests that the size of the anion alone is probably not the major factor controlling the ratio of high-spin to low-spin species (ionic radii are 1.96 Å for Br^- and 2.19 Å for I^-).[19] On the other hand it appears that very large anions such as BPh_4^- and $[Cr(NH_3)_2(NCS)_4]^-$ lead to smaller room-temperature moments and thus favor the formation of complexes with $^1A_{1g}$ ground states. If we assume that these anions are quasi-spherical (BPh_4^- is tetrahedral and the reineckate anion has a trans-octahedral structure[17]), the effective ionic radii are estimated to be about 4.4 and 4.9 Å, respectively.

It is interesting that although the reineckate salt has a room-temperature moment of nearly 4 μ_B, the Mössbauer spectrum at this temperature shows the presence of only a very small fraction ($\lesssim 5\%$) of high-spin species. On the other hand, at about 150 K the tetraphenylborate complex also has a moment of approximately 4 μ_B, and in this case the Mössbauer spectrum indicates that roughly half of the molecules are in the $^5T_{2g}$ ground state. As König and Kremer[20] have discussed, it seems necessary to assume that at 10*Dq* values near the spin crossover energy extensive mixing of eigenstates and spin–orbit coupling effects lead to a nonzero moment for the $^1A_{1g}$ ground term and temperature-dependent moments for both spin states.

The tetrafluoroborate complexes provide the most dramatic example of the effect of the hydration state of a compound on its spin crossover behavior observed to date. The presence of a second water of crystallization lowers the room-temperature moment by ~0.5 μ_B and that at 80 K from 4.19 to 1.38 μ_B. These results are particularly striking in view of the ease with which the dihydrate can be converted to the monohydrate, after which the μ_{eff} vs. T curve for the monohydrate is obtained once more. The differences in the magnetic data for the two BF_4^- salts are much larger than those found previously for $Fe(pyben)_3(ClO_4)_2{\cdot}xH_2O$ (x = 1, 2)[2] and $Fe(pyim)_3SO_4{\cdot}xH_2O$ (x = 2, 3).[3a]

We have attributed these effects to hydrogen bonding between the lattice water molecules and the imino hydrogen of the imidazole fragment of the ligands.[2] Such hydrogen

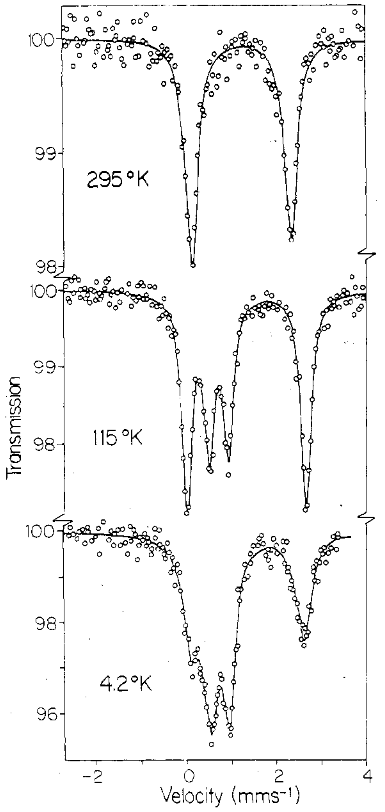

Figure 2. Mössbauer spectra of Fe(pyben)$_3$I$_2$, showing the variation of the high spin:low spin ratio with temperature. In the four-line spectra the outer pair of lines arises from the $^5T_{2g}$ state and the inner pair from the $^1A_{1g}$ state.

bonding would be expected to increase the Bronsted acidity of the NH group, which would in turn strengthen the N → Fe σ bonding by a resonance mechanism[2,21] and produce a net high-spin to low-spin conversion. Further support for the idea that hydrogen bonding plays an important role in determining the details of the $^5T_{2g}$–$^1A_{1g}$ crossover in these complexes comes from two sources. First, most of the ferrous complexes of pyben and pyim which show spin crossover have been isolated in the form of hydrates, and both of these ligands possess an acidic imino hydrogen. On the other hand, anhydrous salts are the rule with other "crossover ligands" such as bpy, phen, and Mephen[13,14,22,23] (Mephen = 2-methyl-1,10-phenanthroline) where no such NH group is present. Second, we have found that addition of trace amounts of strong protonic acids to a reaction mixture in the preparation of a Fe(pyben)$_3^{2+}$ complex invariably yields a compound having a higher μ_{eff} at 80 K than that of the complex obtained when the reaction is carried out at neutral pH.

Mössbauer Data. With the exception of Fe(pyben)$_2$(NCS)$_2$ which is fully high spin between 4.2 and 295 K, all of the other complexes exhibit spin crossover. This is clearly observed in the Mössbauer spectra, where the slow electronic relaxation between the two spin states leads to four-line spectra in the transition region (see Figure 2). The outer pair of lines give Mössbauer parameters typical of high-spin iron(II) salts, while the parameters of the inner pair are typical of low-spin iron(II) species. The spectra show complete thermal reversibility, in the sense that at a given temperature the relative areas of the two pairs of lines are independent of whether that temperature was achieved by cooling or warming the sample.

The relative numbers of molecules with either $^5T_{2g}$ or $^1A_{1g}$ ground states at a given temperature can be estimated approximately from the fraction of the total Mössbauer spectral area contributed by the lines arising from that state. König and co-workers[24-26] have recently measured Debye–Waller factors f for both ground states in several iron(II) complexes showing $^5T_{2g}$–$^1A_{1g}$ transitions. In every case $f(^1A_{1g})$ was found to be greater than $f(^5T_{2g})$. If the same is true here, and this seems likely, then an "area fraction" defined as $A(^5T_{2g})/A(\text{total})$ will underestimate the true fraction of high-spin species present at a given temperature. Such "area fraction" data are included with Mössbauer isomer shifts δ, quadrupole splittings $|\Delta E_Q|$, and line widths Γ in Table I. As can be seen from this table, although the area fractions differ substantially from one compound to another, there do not appear to be any really significant differences in either δ or $|\Delta E_Q|$ values within this series of compounds. For a $^5T_{2g}$ ground state[27] the magnitude and temperature dependence of ΔE_Q are usually quite sensitive to small changes in crystal field distortions,[6] suggesting that such distortions are very similar in all the Fe(pyben)$_3^{2+}$ complexes.

It is interesting that in no case does the area fraction take all permitted values from zero to unity in the temperature range 4.2–295 K. That is, the change in ground state is never complete within this interval of temperature. Fe(pyben)$_3$[Cr(NH$_3$)$_2$(NCS)$_4$]$_2$ remains almost completely low spin at 295 K. The Mössbauer spectrum at this temperature shows an extremely weak absorption at ~2.3 mm s^{-1}, the intensity of which is less than 5% that of the lines arising from the $S = 0$ species, but we were unable to fit the spectrum to four lines. Of the other complexes in this series, Fe(pyben)$_3$(BF$_4$)$_2$·2H$_2$O and the previously studied[2] Fe(pyben)$_3$(ClO$_4$)$_2$·2H$_2$O are the only ones which are fully in the $^1A_{1g}$ state at 4.2 K. Moreover, in all the complexes the area fractions show no significant changes below 80 K. These results are similar to those obtained[22,23] for Fe(Mephen)$_3^{2+}$ derivatives, where König et al.[22,23] have suggested that only part of the molecules are involved in the $^5T_{2g}$–$^1A_{1g}$ transition and that the remainder have permanently paramagnetic ground states.

It should be pointed out that neither the area fraction nor the effective magnetic moment follows a Boltzmann distribution for *any* of the Fe(pyben)$_3^{2+}$ complexes we have studied. Although crossover phenomena of the type observed here are sometimes referred to as "spin equilibria", we think such terminology should be avoided since it is likely to be confusing. If the transition were indeed an equilibrium process, one could define an equilibrium constant

$$K_{\text{eq}} = [\text{high spin}]/[\text{low spin}]$$

and a plot of ln K_{eq} vs. $1/T$ should be linear. This is not the case for any of these complexes nor for many other derivatives showing spin crossover.[22,23,26]

The differences in the Mössbauer area fractions for the two tetrafluoroborate complexes are as striking as the differences in their magnetic moments. The dihydrate is fully low spin at ~130 K and below, whereas for the monohydrate only about half the molecules are in the low-spin state at 4.2 K. The $|\Delta E_Q|$ values for the $S = 2$ states are slightly smaller for the dihydrate than for the monohydrate, but the opposite appears true for the $S = 0$ states. The reasons for these small differences are not obvious, but we shall discuss the quadrupole splitting parameters in relation to the bonding and structure of the cations in more detail below.

From Table I it is seen that Fe(pyben)$_3$(NCS)$_2$·H$_2$O shows a limited spin crossover below ~170 K, while Fe(pyben)$_2$(NCS)$_2$ remains fully high spin down to 4.2 K. Of the anions used in this study NCS$^-$ lies highest in the spectrochemical series; i.e., it is the strongest field ligand and, when coordinated directly to iron as in Fe(pyben)$_2$(NCS)$_2$, might be expected to enhance the low-spin character of the ferrous ion by increasing 100*Dq*. Indeed, the electronic spectra (see also ref 2) indicate that 10*Dq* is in fact slightly larger in the high-spin

Table I. ^{57}Fe Mössbauer Parameters for the Complexes[a]

		$S = 0$				$S = 2$				Area fraction
	T, K	δ^b	ΔE_Q	Γ_1	Γ_2	δ^b	ΔE_Q	Γ_1	Γ_2	($^5T_{2g}$/total)
$Fe(pyben)_3I_2$[c]	4.2	0.75	0.43	0.25	0.25	1.37	2.53	0.28	0.26	0.40
	80	0.74	0.41	0.26	0.26	1.37	2.65	0.27	0.27	0.43
	115	0.74	0.42	0.26	0.26	1.36	2.65	0.27	0.27	0.59
	130	0.75	0.39	0.26	0.26	1.36	2.64	0.27	0.27	0.64
	160	0.72	0.41	0.26	0.26	1.35	2.60	0.28	0.29	0.74
	190	0.70	0.37	0.26	0.26	1.34	2.53	0.30	0.28	0.84
	220	0.76	0.34	0.26	0.26	1.31	2.46	0.28	0.29	0.88
	295					1.27	2.20	0.32	0.32	1.00
$Fe(pyben)_2(NCS)_2$	4.2					1.43	2.55	0.35	0.35	1.00
	115					1.42	2.58	0.30	0.28	1.00
	295					1.32	1.89	0.30	0.28	1.00
$Fe(pyben)_3(NCS)_2 \cdot H_2O$	4.2	0.76	0.46	0.27	0.27	1.41	2.56	0.32	0.33	0.89
	40	0.76	0.46	0.27	0.27	1.41	2.65	0.30	0.35	0.89
	84	0.77	0.44	0.27	0.27	1.40	2.65	0.29	0.32	0.89
	105	0.74	0.49	0.27	0.27	1.35	2.62	0.28	0.30	0.89
	115	0.76	0.47	0.27	0.27	1.37	2.61	0.28	0.30	0.89
	140	0.75	0.46	0.27	0.27	1.38	2.54	0.29	0.29	0.90
	170					1.38	2.42	0.33	0.28	1.00
	200					1.36	2.33	0.33	0.28	1.00
	230					1.35	2.23	0.34	0.30	1.00
	260					1.33	2.13	0.33	0.30	1.00
	294					1.27	2.06	0.33	0.30	1.00
$Fe(pyben)_3(BF_4)_2 \cdot H_2O$	4.2	0.75	0.44	0.23	0.24	1.36	2.56	0.28	0.32	0.52
	86	0.75	0.42	0.23	0.24	1.36	2.67	0.30	0.29	0.53
	100	0.74	0.40	0.23	0.24	1.36	2.65	0.30	0.29	0.61
	130	0.74	0.40	0.24	0.23	1.35	2.62	0.31	0.32	0.67
	160	0.73	0.40	0.27	0.25	1.34	2.59	0.32	0.34	0.71
	190	0.70	0.39	0.26	0.26	1.31	2.54	0.32	0.35	0.77
	220	0.67	0.37	0.28	0.31	1.30	2.44	0.32	0.35	0.83
	250	0.58	0.29	0.24	0.25	1.28	2.34	0.34	0.36	0.89
	295	0.59	0.26	0.25	0.25	1.24	2.17	0.36	0.36	0.88
$Fe(pyben)_3(BF_4)_2 \cdot 2H_2O$	115	0.73	0.50	0.29	0.25					0
	130	0.73	0.48	0.29	0.25					0
	160	0.72	0.47	0.28	0.26	1.29	2.34	0.30	0.31	0.11
	190	0.71	0.46	0.28	0.25	1.29	2.34	0.31	0.30	0.11
	220	0.71	0.46	0.28	0.25	1.31	2.36	0.30	0.30	0.13
	250	0.68	0.43	0.30	0.26	1.27	2.17	0.30	0.31	0.21
	273	0.68	0.38	0.29	0.28	1.24	2.10	0.30	0.30	0.35
	295	0.67	0.42	0.29	0.29	1.21	1.83	0.31	0.30	0.61
$Fe(pyben)_3(BPh_4)_2 \cdot H_2O$	4.2	0.75	0.36	0.29	0.24	1.36	2.55	0.39	0.40	0.33
	87	0.74	0.34	0.30	0.27	1.35	2.67	0.38	0.39	0.34
	100	0.72	0.33	0.30	0.30	1.37	2.71	0.39	0.39	0.38
	120	0.74	0.34	0.28	0.25	1.36	2.66	0.36	0.37	0.40
	150	0.71	0.34	0.28	0.26	1.34	2.60	0.36	0.36	0.45
	180	0.72	0.34	0.28	0.26	1.33	2.54	0.35	0.36	0.48
	210	0.67	0.33	0.27	0.25	1.32	2.42	0.35	0.35	0.54
	240	0.66	0.34	0.28	0.25	1.29	2.36	0.36	0.35	0.57
	270	0.64	0.34	0.27	0.25	1.27	2.22	0.36	0.35	0.59
	294	0.57	0.32	0.28	0.26	1.22	2.12	0.35	0.36	0.63
$Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$	115	0.72	0.37	0.27	0.27					0
	295	0.67	0.29	0.28	0.26					$\leqslant 0.05$

[a] Values for isomer shifts δ, quadrupole splittings ΔE_Q, and line widths Γ are in mm s^{-1}. [b] Relative to disodium pentacyanonitrosylferrate(II). [c] pyben = 2-(2′-pyridyl)benzimidazole.

$Fe(pyben)_2(NCS)_2$ than in the $Fe(pyben)_3^{2+}$ complexes showing spin crossover. It is thus clear that the magnitude of 10*Dq* is not in itself a sufficient condition for the occurrence of a $^5T_{2g}$–$^1A_{1g}$ transition. The differences in the two thiocyanate complexes may well be due to hydrogen-bonding effects. In $Fe(pyben)_2(NCS)_2$ there is no possibility of hydrogen-bond formation, while in $Fe(pyben)_3(NCS)_2 \cdot H_2O$ both the NCS^- ions and the H_2O molecule are potentially available for hydrogen bonding to the imino groups of the pyben ligands.

In the previous paper[2] we pointed out that since the pyridine and imidazole nitrogens of the pyben ligand are inequivalent, it is possible in principle for the $Fe(pyben_3)^{2+}$ cation to adopt either a *mer*- or *fac*-octahedral structure. Magnetic perturbation Mössbauer measurements at 295 K on $Fe(pyben)_3(ClO_4)_2 \cdot H_2O$, which is fully high spin at this temperature, and at 80 K on $Fe(pyben)_3(ClO_4)_2 \cdot 2H_2O$, where this complex is fully low spin, confirmed the existence of *mer*-octahedral structures in both cases.[2] Although the Mössbauer data in Table I and those given in ref 2 suggest a very similar structure for the $Fe(pyben)_3^{2+}$ cation regardless of the nature of the anion and the number of waters of crystallization, it seemed advisable to confirm the *mer*-octahedral configuration in the present complexes. We have therefore examined one fully high-spin derivative [$Fe(pyben)_3(NCS)_2 \cdot H_2O$ at 265 K] and two fully low-spin ones [$Fe(pyben)_3(BF_4)_2 \cdot 2H_2O$ and $Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$ at 80 K] in longitudinal

Table II. Results of Magnetic Perturbation Mössbauer Measurements

	Ground terms	T, K	Sign of V_{zz}	η
$Fe(pyben)_3(BF_4)_2 \cdot 2H_2O$	$^1A_{1g}$	80	?	~0.9
$Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$	$^1A_{1g}$	80	?	~0.9
$Fe(pyben)_3(NCS)_2 \cdot H_2O$	$^5B_{2g}$	265	+	~0.5
$Fe(pyben)_2(NCS)_2$	$^5B_{2g}$	120	+	$\leqslant 0.3$

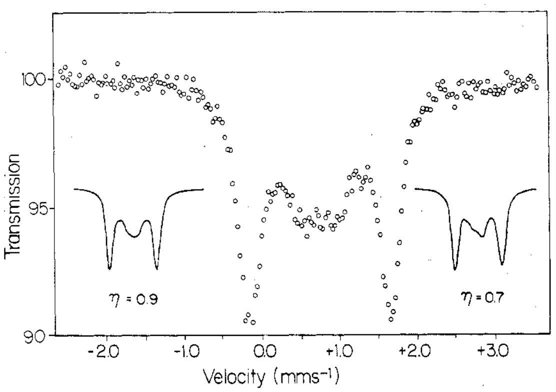

Figure 3. Mössbauer spectrum of $Fe(pyben)_3(BF_4)_2 \cdot 2H_2O$ at 80 K in a longitudinal magnetic field of 50 kG. Computed spectra for $V_{zz} > 0$ and $\eta = 0.7$ and 0.9 are shown in the insets for comparison.

magnetic fields of 50 kG. The results are summarized in Table II.

For the two low-spin complexes the signs of V_{zz}, the principal component of the electric field gradient, cannot be determined with certainty because of the large asymmetry parameters η observed (see Figure 3). The results are clearly consistent with *mer*-octahedral structures, since for a $^1A_{1g}$ ground state the point-charge model perdicts[28] that such a structure should have an indeterminate sign of V_{zz} with $\eta = 1$.

The high-spin ground state may conveniently be discussed in terms of crystal field theory.[2,6] The magnitude and temperature dependence of ΔE_Q for the high-spin species clearly establish that the ground state is an orbital singlet.[6] Now the *fac*-octahedral structure corresponds to a trigonal distortion along the [111] axis of the octahedron, and the orbital ground state will be $|z^2\rangle$. This would produce a negative V_{zz}. On the other hand, the *mer*-octahedral configuration corresponds to a tetragonal distortion, the ground state will be $|xy\rangle$, and V_{zz} will be positive. Moreover, since the two axes normal to the z axis of the electric field gradient will be inequivalent in this structure, there should be a substantial rhombic component of the crystal field and we expect $\eta \neq 0$.

For $Fe(pyben)_3(NCS)_2 \cdot H_2O$ we find $V_{zz} > 0$ and $\eta \simeq 0.5$, which confirms a *mer*-octahedral structure here as well, and that the orbital ground state is $|xy\rangle$. For this reason the ground term has been designated as $^5B_{2g}$ in Table II. Analysis of the temperature dependence of ΔE_Q in terms of a crystal field model[6] indicates the tetragonal and rhombic field splitting parameters $3Ds$ and $12Dr$ are about −340 and −215 cm^{-1}, respectively. These are quite similar to the values found previously[2] for $Fe(pyben)_3(ClO_4)_2 \cdot H_2O$. Moreover, the $10Dq$ values deduced from the electronic spectra (vide supra) are also essentially identical for these two complexes, despite the fact that their spin crossover behavior is very different (see Table I and ref 2). These results indicate that once the field strength of the ligands is appropriate to produce a crossover situation, the finer details of the $^5T_{2g}$–$^1A_{1g}$ transition must depend on factors other than magnitude and symmetry of the ligand field.

The Mössbauer spectrum of $Fe(pyben)_2(NCS)_2$ remains a symmetric doublet down to 4.2 K, and there is no evidence of relaxation broadening of the spectral lines. This shows that the spin–lattice relaxation rate is fast compared to the nuclear Larmor frequency, a situation which is typical of most octahedral high-spin ferrous complexes.[6,29] The usual magnetic perturbation method for determining the sign of V_{zz} is not successful at 4.2 K since the magnetization induced by an applied field is large at this temperature and the effective field at the nucleus is very different from the external field. However, a spectrum of this complex recorded at 120 K in an applied field of 50 kG shows that $V_{zz} > 0$ and η is small, less than about 0.3. Thus the ground state is again the $|xy\rangle$ orbital singlet, but there is a smaller rhombic distortion than in $Fe(pyben)_3(NCS)_2 \cdot H_2O$. This probably reflects the fact that the steric constraints are less severe when there are only two rather than three chelating ligands bonded to the ferrous ion.

Note Added in Proof. Dr. D. M. L. Goodgame has drawn our attention to a paper of which we were previously unaware[30] in which he has reported magnetic moments (at 90 and 295 K) and Mossbauer spectra (in the form of figures only) of four iron(II) derivatives of pyben, viz., $Fe(pyben)_3I_2$, $Fe(pyben)_3(BF_4)_2$, $Fe(pyben)_3(ClO_4)_2$ and $Fe(pyben)_2(NCS)_2$. Unfortunately, the lack of preparative details and analytical data in Goodgame's paper[30] makes comparison with our present results and those of ref 2 difficult. As far as we can judge, our results and those of Goodgame are in substantial agreement for $Fe(pyben)_3I_2$ and $Fe(pyben)_2(NCS)_2$. If we assume the perchlorate complex studied by Goodgame was in fact the dihydrate, his results agree with ours[2] for this compound also. On the other hand, the μ_{eff} value at 90 K quoted[30] for the tetrafluoroborate is significantly higher than we observe for either the mono- or dihydrated form of this salt. It is possible that Goodgame's data pertain to the anhydrous complex. However, we have noted (vide supra and ref 2) that the magnetic properties of these salts are quite sensitive to the method of preparation, and the compound studied by Goodgame may rather have been the monohydrate obtained by a different route from the one reported here.

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Registry No. $Fe(pyben)_3I_2$, 58957-71-4; $Fe(pyben)_3(NCS)_2$, 58957-73-6; $Fe(pyben)_3(BF_4)_2$, 58957-74-7; $Fe(pyben)_3(BPh_4)_2$, 58957-75-8; $Fe(pyben)_3[Cr(NH_3)_2(NCS)_4]_2$, 58957-76-9; $Fe(pyben)_2(NCS)_2$, 52677-34-6.

Supplementary Material Available: Table III giving molar susceptibilities and effective magnetic moments as functions of temperature (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, and University of Wisconsin, Madison, Wisconsin 53706

Spectroscopic Studies of the Structures of Protonated Dieneiron Tricarbonyl Complexes[1a]

MAURICE BROOKHART,*[1b] THOMAS H. WHITESIDES,*[1c] and JOSEPH M. CROCKETT[1b]

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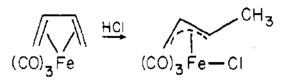
The species generated from protonation of butadieneiron tricarbonyl and cyclohexadieneiron tricarbonyl in strongly acidic media have been studied by infrared and ^{13}C NMR spectroscopy. As previously determined, protonation occurs at iron in these systems to yield monoprotonated metal hydride species. Based on the ^{13}C data reported here, the best description of the bonding between iron and the four-carbon ligand is one in which iron is σ bound to a terminal carbon and π bound to the remaining allyl moiety. ^{13}C spectra are also reported for π-allyliron tetracarbonyl cations which serve as models for the allyl fragment of the σ–π species. Analysis of the ^{13}C–H coupling constants suggests that the metal hydride may be bridging between iron and carbon in the protonated species. Infrared studies support the proposed structures and further suggest that the 16-electron unsubstituted π-allyliron tricarbonyl cation is not generated by ionization of π-allyliron tricarbonyl trifluoroacetate in strongly acidic media (HBF_4–TFA).

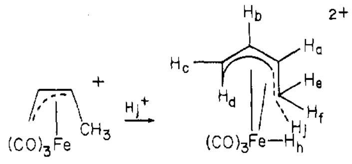
Basic to the elucidation of the reactivity of low-valent polyolefin transition metal complexes is an understanding of their reactions with simple electrophiles, particularly the proton. Investigations of the protonation of simple dieneiron tricarbonyl complexes have revealed a remarkable variety of reactions which depend critically on the exact reaction conditions employed. Protonation of dieneiron tricarbonyl complexes with HCl or HBr where the halide ion is a strongly coordinating anion yields coordinatively saturated π-allyliron tricarbonyl halides.[2] For example, reaction of butadieneiron tricarbonyl, I, with HCl leads to a change in configuration of the diene and production of *syn*-1-methylallyliron tricarbonyl chloride, II.[2b]



I II

In acids with weakly coordinating anions, behavior is somewhat more complex. Gibson[3] has shown that when acyclic dieneiron tricarbonyl complexes are treated with HBF_4 in acetic anhydride at 25 °C, the saturated π-allyliron tetracarbonyl tetrafluoroborate salts could be isolated. Such species are apparently formed from capture of CO by the coordinatively unsaturated π-allyliron tricarbonyl cation. Whitesides[4] has observed similar behavior in trifluoroacetic acid (TFA) and has further shown that in deuterated TFA complete exchange of the terminal protons of the complexed diene occurs before formation of the allyliron tetracarbonyl cation. When cyclohexadieneiron tricarbonyl is treated with TFA, no π-allyl complex is formed; however, Whitesides has demonstrated that the endo protons of the methylene groups undergo rapid and complete exchange in TFA-d_1 at 25 °C.[4] The results demonstrate that protonation of the diene ligand is endo and highly stereospecific (probably through an iron hydride intermediate; see below). In early work Pettit[5] reported isolation of tetrafluoroborate salts of substituted π-allyliron tricarbonyl cations at 25 °C; however, in view of the results of Gibson[3] and Whitesides,[4] it is likely such salts are in fact at least principally the tetracarbonyls.

Young, Holmes, and Kaesz[6] studied by ^1H NMR the low-temperature (−78 °C) protonation of a number of dieneiron tricarbonyl complexes in the highly acidic HSO_3F-SO_2 medium. When the complexes were treated with 1 equiv of acid, a π-allyl species was formed which was presumed to be the unsaturated π-allyliron tricarbonyl cation. Upon addition of excess acid, a second species was formed which was postulated to be a diprotonated species. The structure of this diprotonated species is illustrated as structure IV for butadieneiron tricarbonyl; its formation was presumed to occur by attack of the second proton H_j on the saturated carbon of the π-allyl complex III with shift of H_h from saturated carbon to iron. The low-temperature (−80 °C) ^1H NMR spectrum of IV revealed an iron hydride at τ 24.59 and one-proton signals at τ 3.05 (H_a), 3.56 (H_b), 6.37 (H_c), 8.33 (H_d), 9.00 (H_e), and 10.96 (H_f). Measured coupling constants were $J_{fh} = 22$, $J_{eh} = 14$, $J_{bd} = 11.7$, $J_{cd} = 3.7$, $J_{bc} = 7.8$, $J_{ab} = 6.5$, and $J_{ef} \simeq 7$ Hz. The H_j proton was proposed to be in rapid equilibrium with solvent acid and thus not observed in the ^1H NMR spectrum. At higher temperatures the ^1H NMR signals assigned to H_e, H_f, and H_h broaden and eventually merge to a single resonance, indicating rapid intramolecular scrambling of these three protons. This scrambling was presumed to occur via deprotonation back through species III as an intermediate in which the three protons of the methyl group become equivalent.



III IV

Brookhart and Harris[7] have recently offered an alternative interpretation of the results of Kaesz.[6] The initially generated species (III) was proposed to be a covalent fluorosulfonate, V. In the presence of excess acid ionization of the fluorosulfate ligand occurs. The final species formed was postulated to be *mono*protonated VI rather than diprotonated IV. In structure VI, iron is π bound to an allyl fragment and σ bound to a terminal carbon. This can be viewed as arising from the oxidative addition of a C–H bond of the methyl group to iron. In the formation of VI, the unsaturated π-allyliron tricarbonyl