

scheme one would derive from crystal field theory in D_{4h} symmetry.

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A Study of the Electronic and Structural Properties of Bis(pyridine)dichloroiron(II)

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Bis(pyridine)dichloroiron(II), $\text{Fe}(\text{py})_2\text{Cl}_2$, has been prepared by two different methods. The structure of the material at room temperature has been shown to be polymeric and to possess two symmetric bridging chloride ligands which are equivalently bonded between two iron atoms. On the basis of the Mössbauer spectral properties of the two preparations, it has been concluded that the crystalline material undergoes a transformation at lower temperatures to a polymeric structure containing asymmetric bridging chloride ligands. The magnetic and electronic spectral properties of these materials have been measured and the results are discussed in terms of the proposed structural change at low temperature.

Introduction

Several papers have been published¹ which deal with the electronic properties of the pyridine complexes containing iron(II) halides of stoichiometry $\text{Fe}(\text{py})_4\text{X}_2$, but relatively little attention has been given to the detailed electronic properties of the complexes of stoichiometry $\text{Fe}(\text{py})_2\text{X}_2$. Gill, *et al.*,² recorded the room-temperature magnetic moment of $\text{Fe}(\text{py})_2\text{Cl}_2$ as 5.75 BM and concluded on the basis of its X-ray powder pattern that the complex possesses a polymeric octahedral structure. Goodgame, *et al.*,^{1a} investigated the electronic spectral bands for $\text{Fe}(\text{py})_2\text{Cl}_2$ but did not describe the method which they used for its preparation. Clark and Williams³ measured the infrared spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ but were unable to assign the metal-ligand vibrational bands. The purpose of this paper is to present the experimental results of an investigation of the spectral and magnetic properties of $\text{Fe}(\text{py})_2\text{Cl}_2$ and discuss these results in terms of a proposed temperature-dependent structural model.

Experimental Section

Synthesis of Compounds.— $\text{Fe}(\text{py})_4\text{Cl}_2$ was prepared by following essentially the same procedure as previously reported⁴ except that all manipulations were carried out under a stream of dry nitrogen gas. *Anal.* Calcd for $\text{FeC}_{20}\text{H}_{20}\text{N}_2\text{Cl}_2$: C, 54.20; H, 4.55; N, 12.64. Found: C, 53.87; H, 4.47; N, 12.48.

$\text{Fe}(\text{py})_2\text{Cl}_2$.—(A) This compound was prepared by rapidly adding, while stirring, a concentrated solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in deoxygenated anhydrous methanol to a deoxygenated solution of approximately 50% freshly distilled pyridine in anhydrous methanol. The addition was carried out under a stream of dry nitrogen gas to prevent oxidation of the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution. When the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution was added, a deep yellow color immediately formed, and golden yellow crystals precipitated within 3–5 min. The precipitate was filtered *via* suction under

nitrogen and was washed first with a small amount of cold deoxygenated absolute ethanol and then with cold deoxygenated absolute ether. This procedure must be closely followed. If the complex does not precipitate within about 5 min, $\text{Fe}(\text{py})_4\text{Cl}_2$ will form and precipitate over a period of several hours. No difficulty was experienced in reproducing this preparation.

A completely dry sample of $\text{Fe}(\text{py})_2\text{Cl}_2$ is relatively stable with respect to air oxidation and can be stored for a period of several weeks without apparent decomposition in a desiccator which is filled with dry nitrogen. *Anal.* Calcd for $\text{FeC}_{10}\text{N}_{10}\text{Cl}_2$: C, 42.15; H, 3.54; N, 9.83. Found: C, 41.96; H, 3.53; N, 9.73.

(B) An alternate preparation of $\text{Fe}(\text{py})_2\text{Cl}_2$ involved decomposing $\text{Fe}(\text{py})_4\text{Cl}_2$ in a drying pistol, which was heated to 65° and subjected to continuous evacuation for a period of approximately 1 hr. This evacuation produced a loss of 49.8–50.2% of the original pyridine, as determined by weight loss measurements. The resulting sample of $\text{Fe}(\text{py})_2\text{Cl}_2$ was found to be stable. *Anal.* Found: C, 42.23; H, 3.67; N, 9.89.

Physical Measurements.—All electronic spectra were recorded on a Cary 14 spectrophotometer. To make the measurements, the solid samples were milled with Kel-F No. 90 grease and placed between quartz plates.

The Mössbauer spectral results were obtained with an Austin Science Associates constant-acceleration spectrometer. The spectrometer was calibrated by using natural iron foil, and the source was maintained at room temperature for all measurements. The low-temperature results were obtained with a liquid nitrogen cryostat that has a sample holder which protects the polycrystalline sample from the cryostat vacuum. The National Bureau of Standards Parlor computer program⁵ was used to evaluate the spectral results. The error limits for the results that are recorded in Table I are less than or equal to ± 0.05 mm/sec, as calculated from the variance of the final computer iteration.⁵ All magnetic measurements were made on a Faraday magnetic susceptibility balance described by Long.⁶ The balance was calibrated by using $\text{CoHg}(\text{NCS})_4$, and the sample temperature was measured with a platinum resistance thermometer. All magnetic moments were measured at three field strengths. In some cases (noted below) these moments exhibited a field dependence. The error limits for the magnetic moments that are recorded in Table II are ± 0.05 BM at higher temperatures (above 150°K) and are ± 0.10 BM at the lower temperatures.

All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

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TABLE I
MÖSSBAUER SPECTRAL PARAMETERS

Compd	Temp, °K	ΔE_Q , mm/sec	δ^a , mm/sec	Γ^b , mm/sec
Fe(py) ₄ Cl ₂	78	3.53	1.14	0.25
	195	3.42	1.09	0.25
	300	3.15	1.05	0.25
Fe(py) ₂ Cl ₂ (A)	78	1.28	1.20	0.26
	300	0.56	1.07	0.24
Fe(py) ₂ Cl ₂ (B)	78	0.63	1.21	0.25
		1.27	1.21	0.27
	195	0.55	1.13	0.23
		1.15	1.13	0.27
	273	0.56	1.09	0.24
	300	0.57	1.06	0.24

^a Relative to natural iron foil. ^b Full line width at half-maximum intensity.

TABLE II
MAGNETIC DATA

Fe(py) ₂ Cl ₂ (A)			Fe(py) ₂ Cl ₂ (B)		
Temp, °K	10 ⁶ χ _M , cgsu	μ _{eff} , BM	Temp, °K	10 ⁶ χ _M , cgsu	μ _{eff} , BM
21.3	813,000	11.77 ^a	28.2	316,200	8.44 ^a
28.0	411,700	9.60 ^a	33.2	216,200	7.58 ^a
70.3	68,100	6.19 ^a	48.2	107,700	6.44
98.0	42,900	5.80	66.5	68,010	6.01
134.0	29,890	5.66	88.7	47,980	5.83
178.5	21,500	5.54	110.0	37,420	5.74
231.8	15,520	5.36	131.5	30,530	5.67
248.5	14,520	5.37	153.5	25,420	5.59
270.5	13,240	5.35	178.8	21,650	5.56
291.0	12,230	5.33	199.5	19,210	5.54
			224.0	17,000	5.52
			247.5	15,450	5.53
			270.5	13,680	5.44
			288.5	12,690	5.41

^a Field-dependent values of μ_{eff}. The highest magnetic field values are reported.

Results and Discussion

The X-ray powder patterns for Fe(py)₂Cl₂ (A) and Fe(py)₂Cl₂ (B) were measured at room temperature and were found to be identical with each other and with the powder pattern for Co(py)₂Cl₂. Dunitz,⁷ who studied Co(py)₂Cl₂, reported that its crystal is monoclinic (space group *P2/b*) and that its structure contains polymeric chains which consist of symmetric bridging chloride ligands (Co-Cl distance, 2.49 Å; Cl-Co-Cl bond angle, 85.5°) that occur between approximately octahedrally coordinated cobalt atoms. On the basis of the powder patterns, the authors conclude that at room temperature both preparations of Fe(py)₂Cl₂ possess polymeric octahedral coordination about the iron atom, have symmetric bridging chloride ligands, and are isostructural with Co(py)₂Cl₂.

The infrared spectra (400–4000 cm⁻¹) of Fe(py)₂Cl₂ (A) and Fe(py)₂Cl₂ (B) are identical except for minor differences in band intensities and are very similar to the spectrum for Fe(py)₄Cl₂. The only distinct difference between the Fe(py)₄Cl₂ and Fe(py)₂Cl₂ bands is that an absorption at 690 cm⁻¹—most likely a CH deformation⁸—for the latter compound is significantly broadened.

The Mössbauer spectral results for Fe(py)₂Cl₂ are presented in Table I, which also includes for comparison the spectral parameters for Fe(py)₄Cl₂. The results for the tetragonally distorted octahedral

Fe(py)₄Cl₂ compound agree closely with previously published results.^{1b,c} The temperature dependence of the parameters will be discussed in a later publication.⁹ For each of the compounds listed in Table I, the chemical isomer shifts, δ, and line widths, Γ, are consistent with the values expected for an iron(II) ion in a distorted octahedral, weak ligand field complex.^{1b,10} The values for ΔE_Q, the quadrupole splitting, require special comment. The experimental Mössbauer spectrum of Fe(py)₂Cl₂ (B) is shown at room temperature in Figure 1 and at 78°K in Figure 2. In these figures, the solid lines represent the best theoretical computer fit which could be obtained by assuming Lorentzian functions for the Mössbauer absorption lines.⁵ The spectrum of Fe(py)₂Cl₂ (A) at room temperature is very similar to the spectrum shown in Figure 1. The compound Fe(py)₂Cl₂ (A) exhibits only two lines at 78°K. In all cases, the Mössbauer spectrum of Fe(py)₂Cl₂ exhibits no lines which may be attributed to Fe(py)₄Cl₂.

The quadrupole splitting in Fe(py)₂Cl₂ (A) is much lower than that observed in Fe(py)₄Cl₂ indicating a significantly lower electric field gradient (EFG) in the former complex. This lower EFG and the resultant reduction in ΔE_Q with temperature in going from room temperature to 78°K are large but can be explained on the basis of the simple crystal field model¹¹ if the reduction from octahedral symmetry about the iron atom is small. No attempt is made in this note to evaluate the magnitude of the EFG for reasons to be detailed in a later publication.⁹

The Mössbauer spectrum of Fe(py)₂Cl₂ (B) is unusual in that at 195 and 78°K it exhibits four absorption lines as opposed to the two lines shown by Fe(py)₂Cl₂ (A). The cause of the lines in the spectrum of the former complex is interpreted by the authors as being due to iron atoms in two slightly different chemical environments, both of which have nonzero but differing electric field gradients. Based upon line intensity considerations, the inner lines are interpreted as being a result of one of the chemical environments while the outer lines are a result of the second environment. The parameters shown in Table I are based upon this interpretation. It is interesting to note that each set of lines exhibits the same chemical isomer shift at 78 and 195°K. This indicates that the two different chemical environments provide the same s-electron densities at the respective surfaces of the iron nuclei in the two different sites. The outer set of lines observed at low temperatures corresponds to the same chemical environment observed in Fe(py)₂Cl₂ (A) at low temperatures. The appearance of the additional set of inner lines in the spectrum of Fe(py)₂Cl₂ (B) at low temperatures is completely reversible with temperature and is reproducible with only slight changes in intensity ratios from preparation to preparation. The relative areas of the four observed lines are 0.21, 0.30, 0.30, and 0.20 at 78°K and 0.17, 0.35, 0.35, and 0.14 at 195°K. A structural model is proposed below which accounts for the large temperature dependence of ΔE_Q for preparation (A) and the additional absorptions observed in (B) at low temperatures.

The magnetic susceptibilities of both preparations

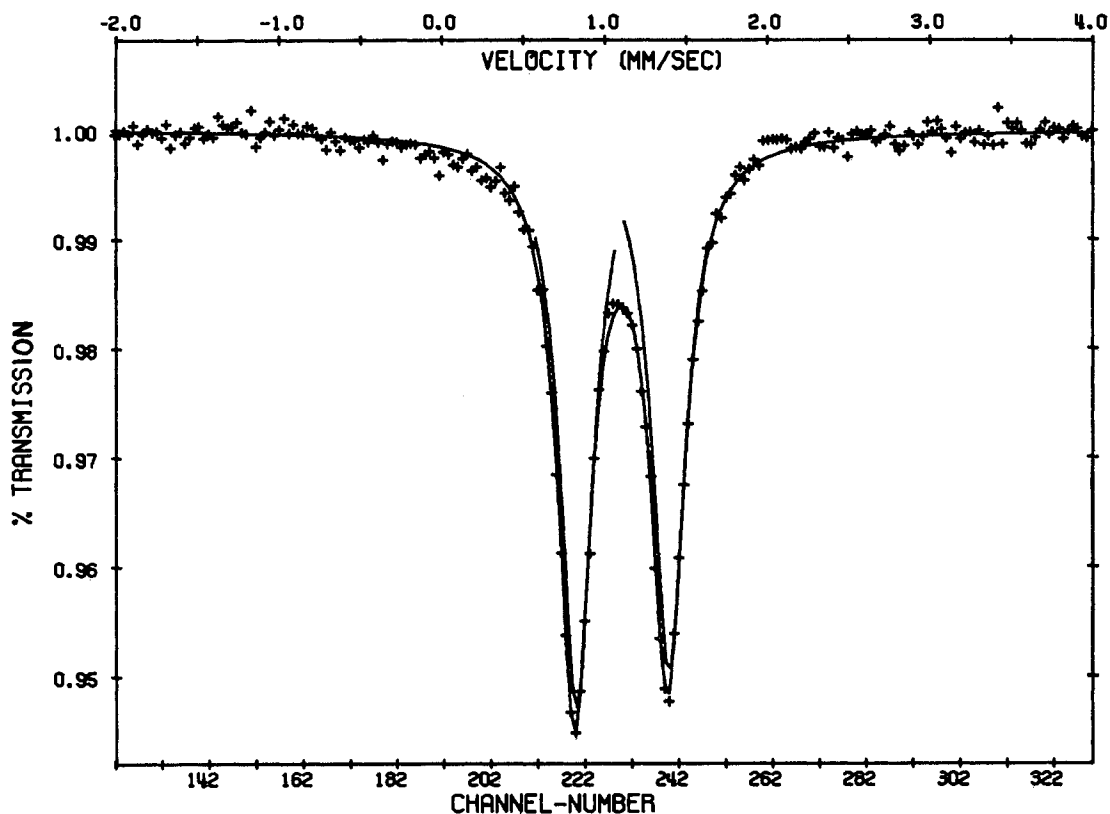
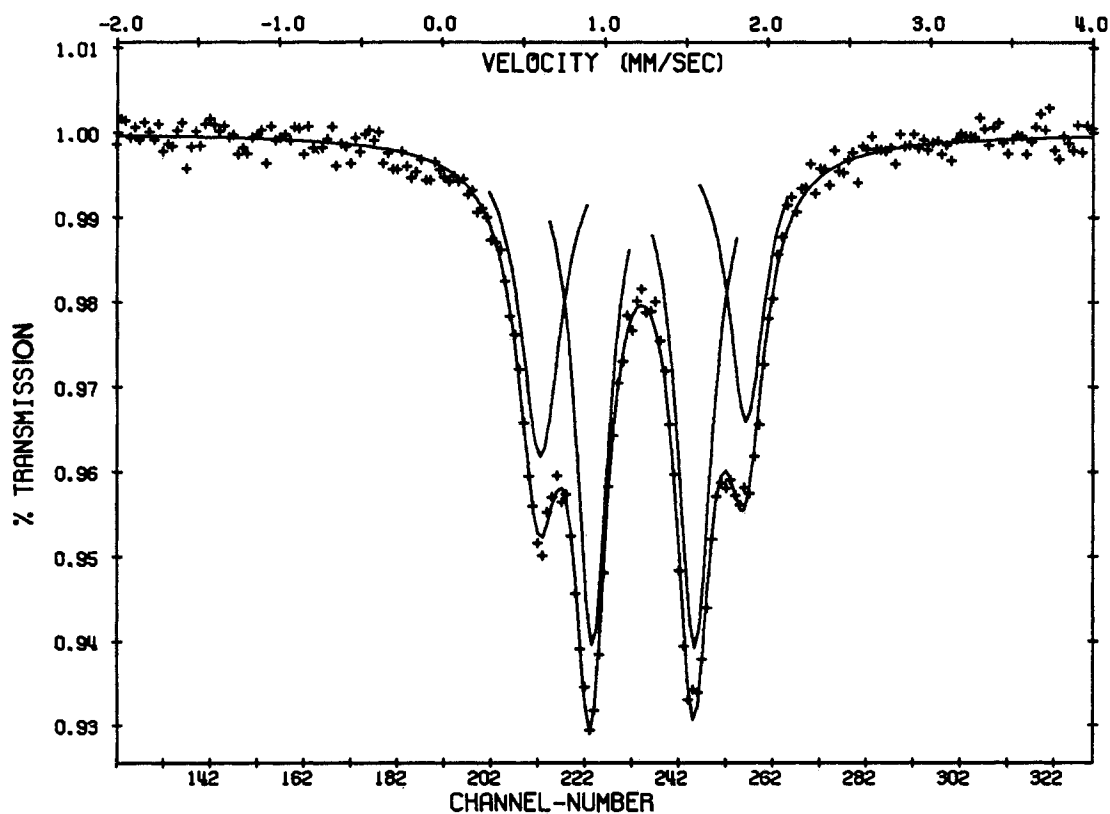
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Figure 1.—Mössbauer effect spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ (B) at room temperature.Figure 2.—Mössbauer effect spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ (B) at 78°K.

of $\text{Fe}(\text{py})_2\text{Cl}_2$ have been studied from room temperature down to 20°K and the results are given in Table II and in Figure 3. The results for the two preparations are essentially the same at all temperatures and above 100°K are consistent with theoretically predicted

values of μ_{eff} for distorted octahedral high-spin iron(II) complexes.^{6,12} At temperatures below about 100°K, the magnetic moment, in disagreement with the theo-

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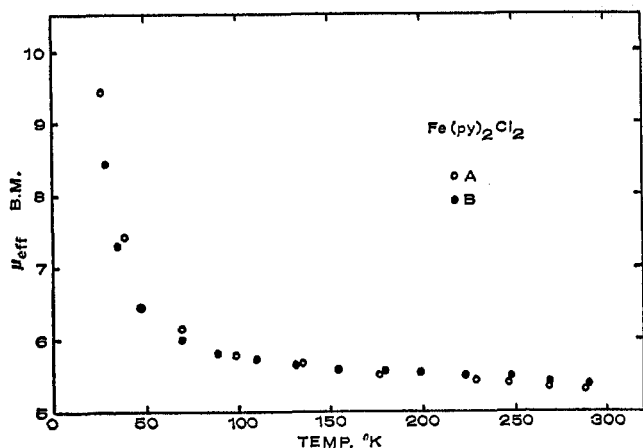


Figure 3.—Magnetic moment *vs.* temperature for $\text{Fe}(\text{py})_2\text{Cl}_2$.

retical model,¹² begins to increase with decreasing temperature. At the lower temperatures (see Table II) the calculated moments show field dependence. Although these field-dependent magnetic moments

the model of ferromagnetic exchange proposed by Anderson^{13,14} and discussed in detail below.

The electronic absorption spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ (A) is shown in Figure 4 which also includes the spectrum of $\text{Fe}(\text{py})_4\text{Cl}_2$ for comparison. The absorption spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ (B) is identical with that of preparation (A) except that minor variations in the relative intensity of the low-energy band occur in some preparations of (B). Each compound exhibits identical sharp bands at 5992, 4665, 4613, 4554, 4519, and 4447 cm^{-1} that are assigned as overtones of pyridine vibrational bands. The spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ consists of a broad symmetric band at 9750 cm^{-1} and a second broad band at 5900 cm^{-1} . These bands are assigned, respectively, to the electronic transitions from the ground state (either the 5E_g or the ${}^5B_{2g}$ state in D_{4h} symmetry resulting from the ${}^5T_{2g}$ state in O_h symmetry) to the ${}^5A_{1g}$ state and to the ${}^5B_{1g}$ state (which arise in D_{4h} symmetry from the 5E_g excited state in O_h symmetry). These assignments agree with those of Goodgame, *et al.*,^{1a} and indicate that, as expected from the positions of the ligands in the spectrochemical

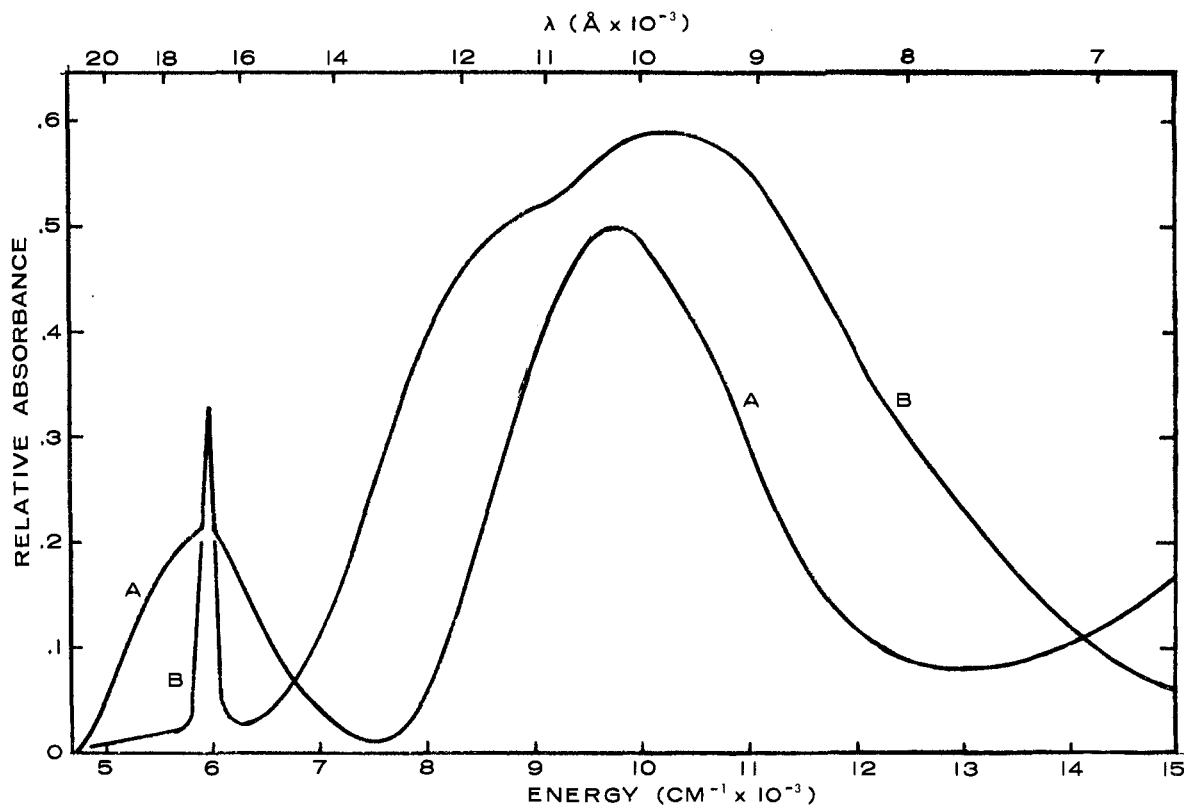


Figure 4.—Electronic spectra at room temperature: A, $\text{Fe}(\text{py})_2\text{Cl}_2$ (A); B, $\text{Fe}(\text{py})_4\text{Cl}_2$.

have no theoretical significance, they have been included in Table II and in Figure 3 for comparison. The observed field dependence and sharp increase in μ_{eff} at low temperatures could be the result of an impurity which has a Curie temperature of the order of 100°K or could result from a true ferromagnetic spin-spin coupling—through the bridging chloride ligand—of the unpaired electron spins on adjacent iron atoms in the polymeric chain of the complex. It is impossible at this time to distinguish experimentally between the two possibilities, but the latter case is consistent with

series, the in-plane ligand field strength is weaker for $\text{Fe}(\text{py})_2\text{Cl}_2$ than for $\text{Fe}(\text{py})_4\text{Cl}_2$.

On the basis of the above experimental evidence, it can be concluded that the solid-state structure of $\text{Fe}(\text{py})_2\text{Cl}_2$ is temperature dependent. The structure at room temperature has been shown by the above-discussed X-ray studies to possess two symmetric bridging chloride ligands (per iron atom) which are

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equivalently bonded between two iron atoms. At some temperature between 195 and 273°K, or perhaps over a range of temperatures, the crystal undergoes a transformation to a structure containing asymmetric bridging chloride ligands. It is possible that this asymmetric structure at low temperatures is similar to the structure of $\text{Cu}(\text{py})_2\text{Cl}_2$, which has been studied in detail by Dunitz⁷ and found to possess asymmetric bridging chloride ligands (Cu-Cl distances, 2.28 and 3.05 Å; Cl-Cu-Cl bond angle, 88°). This structural change accounts for the Mössbauer spectral results for $\text{Fe}(\text{py})_2\text{Cl}_2$ (A) because the decrease in symmetry about the iron atom with decreasing temperature would result in a large EFG and, hence, larger ΔE_Q but would not necessarily change the total s-electron density at the iron nucleus. The additional set of lines observed in the Mössbauer spectrum of $\text{Fe}(\text{py})_2\text{Cl}_2$ (B) at low temperatures can now be attributed to a portion of the polycrystalline sample which does not undergo this structural transformation and which retains the symmetric bridging structure at low temperature. This results in a smaller EFG for this particular portion of the sample and produces the additional low ΔE_Q value observed at low temperatures. The method of preparing $\text{Fe}(\text{py})_2\text{Cl}_2$ (B) *via* the decomposition of $\text{Fe}(\text{py})_4\text{Cl}_2$ probably produces a crystal which has a large number of "defects." A high concentration of these "defects" possibly prevents a portion of the polycrystalline sample from undergoing the proposed crystal transformation at lower temperatures. If this is the case, the chemical isomer shift for each set of lines would be expected to be the same.

The proposed structural change is also consistent with the magnetic properties observed for $\text{Fe}(\text{py})_2\text{Cl}_2$. Anderson^{13,14} has proposed a model for magnetic exchange (through a bridging atom) between paramagnetic metal ions, which, for the case under study, predicts ferromagnetic exchange if (1) the iron ions and chloride bridging ligands lie in the same plane, (2) the Fe-Cl-Fe and Cl-Fe-Cl bonding angles do not differ greatly from 90°, and (3) the bonds between the

bridging chloride ligand and the iron ions consists predominantly of chlorine p orbitals and iron d orbitals. Assuming that requirements 1 and 3 are met—which seems reasonable—it is clear that as the Cl-Fe-Cl bond angle approaches 90° the model predicts ferromagnetic exchange. $\text{Fe}(\text{py})_2\text{Cl}_2$ is shown from the above-discussed X-ray work to have a Cl-Fe-Cl bond angle of 85.5° at room temperature. If the proposed asymmetric structure at low temperature is similar to $\text{Cu}(\text{py})_2\text{Cl}_2$,⁷ then its Cl-Fe-Cl bond angle will be of the order of 88°. This increase in bond angle toward 90° at lower temperatures results in the increasing possibility of ferromagnetic exchange which is indeed observed at temperatures below about 100°K. If the model proposed by Anderson^{13,14} is valid for this system, it would appear that the structural transformation occurs over a range of temperatures since no discontinuous change is observed (see Figure 3) in the magnetic moment of either sample of $\text{Fe}(\text{py})_2\text{Cl}_2$. Of course, the possibility of "ferromagnetic impurities" still cannot be ruled out experimentally.

The authors conclude that the experimental properties of $\text{Fe}(\text{py})_2\text{Cl}_2$ presented above are consistent with a temperature-dependent crystalline structure. They further conclude that $\text{Fe}(\text{py})_2\text{Cl}_2$ contains symmetric bridging chloride ligands at room temperature and asymmetric bridging chloride ligands at temperatures of 195°K and lower. More detailed X-ray structural studies on $\text{Fe}(\text{py})_2\text{Cl}_2$ at low temperatures and Mössbauer spectral studies at intermediate temperatures are planned hopefully to provide additional evidence in support of the proposed structural transformation.

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1,2-Dithiolene Complexes of Ruthenium and Iron

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Physical characterization and chemical reactivity of $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$, the initial product of the reaction between iron pentacarbonyl and bis(perfluoromethyl)dithietene, are reported. Bis(perfluoromethyl)dithietene reacts with triruthenium dodecacarbonyl at 100° to give an orange, carbonyl-containing substance and at higher temperatures to give a green, carbonyl-free material. Purification of the two substances has not been achieved. Reaction of the orange material with group V bases yields species of the type $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}(\text{CO})_n(\text{ER}_3)_{3-n}$. The green material reacts with group V bases to yield $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$ and $(\text{base})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$ (base = $(\text{C}_6\text{H}_5)_3\text{P}$, $(\text{C}_6\text{H}_5)_3\text{As}$, $(\text{C}_6\text{H}_5)_3\text{Sb}$). Magnetic, electrochemical, and electronic spectral characteristics of these new compounds are reported.

Introduction

A variety of novel products have been obtained from the reaction of bis(perfluoromethyl)dithietene and

metal carbonyls.¹ As part of a study of the synthesis and properties of polynuclear dithiolene complexes, the reactions of bis(perfluoromethyl)dithietene with

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