

Figure 3. Mossbauer spectrum of $\text{Fe}(\text{phenanthroline})_2(\text{NCS})_2$ at 300°K and $H_{\text{transverse}} = 20 \text{ kG}$.

of $\text{Fe}(\text{phen})_2\text{X}_2$ via the replacement of one bidentate phenanthroline in the tris (D_3) complex with two monodentate ions to yield the cis (C_{2v}) complex, then the right side of Figure 2 applies. In the presence of this additional low-symmetry (C_{2v}) ligand field component, the sixth d electron still occupies the d_{z^2} orbital and the complex has a 5A ground state. In this instance, relative to the tris(2-chlorophenanthroline) and -(2-methylphenanthroline) complexes, a larger negative quadrupole splitting is expected and observed. This is

illustrated in Figure 3 for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ in which the quadrupole splitting at 300°K is found to be -2.67 mm/sec . A similar situation¹⁶ exists for pairs of low-spin iron(III) complexes such as $[\text{Fe}(\text{phen})_3]^{3+}$ and $\text{cis-}[\text{Fe}(\text{phen})_2(\text{CN})_2]^+$ where V_{zz} is positive for both complexes and corresponds to a hole in the d_{z^2} orbital in each case.

In conclusion it is worthwhile to point out that the temperature dependence of powder magnetic susceptibilities⁷ and quadrupole splittings¹² for high-spin $\text{Fe}(\text{diimine})_2\text{X}_2$ complexes generally correlate with orbitally nondegenerate ground electronic states. The advantage of perturbed Mossbauer spectroscopy is that it distinguishes between a ground-state orbital singlet wave function composed primarily of the d_{xy} orbital (a 5B ground state) and one composed primarily of the d_{z^2} orbital (a 5A ground state).

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Mossbauer, Electronic, and Structural Properties of Bis(pyridine)dithiocyanatoiron(II). A Ferromagnetically Ordered Polymer

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An interesting example of an extended (lattice) ferromagnet containing three-atom covalent bridging has been characterized. The bis(pyridine)dithiocyanatoiron(II) complex, $\text{Fe}(\text{py})_2(\text{NCS})_2$, has been prepared by thermolysis of the tetrakis complex, $\text{Fe}(\text{py})_4(\text{NCS})_2$. A study of the X-ray, magnetic, and infrared, electronic, and Mossbauer spectral properties of the bis complex has indicated that it contains polymeric, pseudooctahedral, coordination geometry with near linear bridging thiocyanate ligands. The electronic spectrum of the bis complex shows a larger, low symmetry, ligand field than that present in $\text{Fe}(\text{py})_4(\text{NCS})_2$. Unperturbed Mossbauer spectra reveal a larger quadrupole splitting and a smaller isomer shift in the bis complex as compared with the tetrakis complex. The magnetically perturbed Mossbauer spectrum at room temperature shows that the principal component of the electric field gradient tensor is positive and corresponds to a d_{xy} ground orbital. Mossbauer spectra at 4.2°K in zero and longitudinal magnetic fields of up to 80 kG confirm the presence of ferromagnetic ordering. The latter spectra, which have been computer simulated, indicate an internal hyperfine field, H , of 280 kG, a positive axially symmetric electric field gradient, V_{zz} , and an angle, β , of 75° between V_{zz} and H .

Introduction

High-spin iron(II) halide and pseudohalide complexes containing pyridine have been under investigation for many years. Several papers dealing with the electronic and structural properties of the tetrakis pyridine iron(II) halides and pseudohalides have been published.²⁻⁹ A study¹⁰ of the

electronic and structural properties of bis(pyridine)dichloroiron(II) has shown that this complex contains polymeric, pseudooctahedral, coordination geometry with bridging chloride ligands. This same study also revealed a low-temperature structural transformation from a symmetric to an asymmetric iron-chlorine bridging bond. This transformation has been confirmed by several subsequent investiga-

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tors,¹¹⁻¹³ one of whom¹² presented evidence in this complex for a low-temperature (10.5°K) transformation to a ferromagnetic phase.

The $\text{Fe}(\text{py})_2(\text{NCS})_2$ and $\text{Fe}(\text{py})_2\text{Cl}_2$ complexes are particularly interesting when compared with anhydrous FeCl_2 . This latter salt has the CdCl_2 structure¹⁴ and exhibits positive (ferromagnetic) exchange along the



chain, negative (antiferromagnetic) interchain interactions, and "meta-magnetic" behavior.¹⁵ The latter phenomenon is a field-dependent cooperative magnetic behavior. For example, in the case of FeCl_2 , there is a change from overall antiferromagnetic ordering to ferromagnetic (strictly speaking, paramagnetic) ordering at an applied field of ca. 11 kG.¹⁶ The above mentioned pyridine complexes have chloro or thiocyanato intrachain bridging with *trans*-pyridine molecules which are expected to significantly reduce any interchain magnetic interactions. This simplification allows for the possibility of both a lower dimensionality of the magnetic interaction and a very weak meta-magnetic behavior and indeed makes these systems attractive for detailed magnetic study. The thiocyanate complex is also noteworthy in that it serves as an example of a ferromagnetic interaction involving a three-atom covalent bridge. By analogy with other thiocyanate bridged systems,¹⁷ the metal-metal distance is probably too great for strong metal-metal exchange. Thus the magnetic behavior of this complex must be due in a large part to magnetic superexchange through the NCS bridging groups. To our knowledge, the only other examples of ferromagnetic intramolecular coupling with this bridging moiety or, for that matter, with any other multi-atom bridging species are found in the $[\text{Ni}(\text{ethylenediamine})_2(\text{NCS})_2]_2$ dimer¹⁷ in which $J = +5 \text{ cm}^{-1}$ and in the $[\text{Ni}(\text{tren})(\text{NCS})_2]_2(\text{BPh}_4)_2$ and $[\text{Ni}(\text{tren})(\text{NCSe})_2]_2(\text{BPh}_4)_2$ dimers (where tren is 2,2',2''-triaminotriethylamine) in which $J = +2.4$ and $+1.6 \text{ cm}^{-1}$, respectively.¹⁸

Experimental Section

Syntheses of Compounds. The compound $\text{Fe}(\text{py})_2(\text{NCS})_2$ was prepared by the same procedure as previously reported¹⁹ except that all operations were carried out in a Vacuum Atmospheres Inc., inert atmosphere, glove box filled with an argon atmosphere. *Anal.* Calcd for $\text{FeC}_{12}\text{H}_{16}\text{N}_4\text{S}_2$: C, 54.10; H, 4.13; N, 17.21. Found: C, 54.22; H, 4.18; N, 17.11.

$\text{Fe}(\text{py})_2(\text{NCS})_2$ was prepared by thermolysis of $\text{Fe}(\text{py})_4(\text{NCS})_2$ under vacuum at 117° for 10 hr in a Abderhalden drying apparatus. During heating, the sample lost 32.65% of its weight. This loss corresponds to a 50.4% loss of pyridine. During the thermolysis, the yellow crystals of the tetrakis complex changed to pale brown.

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When a small aliquot of $\text{Fe}(\text{py})_2(\text{NCS})_2$ was exposed to the air, it changed to a purple color. The sample of $\text{Fe}(\text{py})_2(\text{NCS})_2$ was stored in a desiccator filled with dry argon. *Anal.* Calcd for $\text{FeC}_{12}\text{H}_{16}\text{N}_4\text{S}_2$: C, 43.65; H, 3.05; N, 16.97. Found: C, 43.68; H, 2.97; N, 16.84.

Physical Measurements. All magnetic measurements were made on a standard Gouy balance which was calibrated with $\text{Hg}[\text{Co}(\text{NCS})_4]$. The sample temperature was measured with a copper-constantan thermocouple, and all magnetic susceptibilities were measured at four different field strengths. The error limits for the reported magnetic moments are $\pm 0.05 \text{ BM}$.

The electronic absorption spectra were recorded by using a Cary 14 spectrophotometer. The spectra were obtained by mulling the compound with Fluorolube Grease, GR-90, between quartz plates. The low-temperature spectra were obtained by using an Air Products and Chemical Inc. AC-2 Cryo-Tip refrigerator. The infrared spectra in the range 4000-400 cm^{-1} were recorded in KBr pellets by using a Perkin-Elmer 180 spectrometer. The far-infrared spectra were obtained with a Perkin-Elmer 301 far-infrared spectrometer both as Nujol mulls and as solids in a diamond cell.

A Siemens Crystalflex IV X-ray diffractometer equipped with a copper tube and a nickel filter was used to obtain the X-ray diffraction powder patterns.

An Austin Science Associates, constant-acceleration, Mossbauer spectrometer was used to obtain the magnetically unperturbed spectral results. The spectrometer was equipped with a copper matrix source which was maintained at room temperature and was calibrated with natural iron foil. All the samples were measured in a vacuum cryostat with a sample holder which protected the sample from the cryostat vacuum. The National Bureau of Standards PARLOR computer program²⁰ was used to evaluate the unperturbed Mossbauer spectral results. The error limits for the reported Mossbauer parameters are less than or equal to $\pm 0.04 \text{ mm/sec}$, as calculated from the variance of the final computer iteration. The low-temperature, magnetically perturbed, Mossbauer spectral measurements were made with a conventional constant acceleration spectrometer. The magnetic field was generated by using a Nb-Sn superconducting magnet, which operated in the persistent mode up to fields of 80 kG. The polarization direction was longitudinal, and both the source and the absorber were at 4.2°K. The longitudinal spectra, which were measured with the samples at ambient temperature, were obtained by using a Westinghouse Nb-Ti superconducting magnet. The source consisted of 100 mCi of ⁵⁷Co in a rhodium matrix.

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

Results and Discussion

The X-ray powder diffraction patterns for $\text{Fe}(\text{py})_2(\text{NCS})_2$, $\text{Fe}(\text{py})_4(\text{NCS})_2$, and $\text{Co}(\text{py})_2(\text{NCS})_2$ have been measured, and crystal *d* spacings are presented in Table I. As can be seen from these results, the two iron compounds are not isomorphous, and the bis complex, within the limits of the X-ray diffraction analysis, is not contaminated with any residual tetrakis complex. The crystal structure of $\text{Fe}(\text{py})_4(\text{NCS})_2$ has been reported by Sotofte and Rasmussen,⁹ who found that the structure contains a *trans* octahedral coordination geometry and has nitrogen-bonded thiocyanate ligands. The two bispyridine complexes are isomorphous, hence the $\text{Fe}(\text{py})_2(\text{NCS})_2$ complex is assigned the polymeric pseudo-octahedral coordination geometry, which has linear bridged thiocyanate groups. This is the structure which has been determined by a single-crystal X-ray study²¹ of $\text{Co}(\text{py})_2(\text{NCS})_2$.

The magnetic susceptibility of $\text{Fe}(\text{py})_2(\text{NCS})_2$ and $\text{Fe}(\text{py})_4(\text{NCS})_2$ has been measured as a function of temperature. The results are presented in Table II. The room-temperature results for the tetrakis complex are in excellent agreement with previously reported values for this complex,^{4,22} whereas the value for the bis complex is signifi-

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Table I. X-Ray Powder Diffraction Data^a

Fe(py) ₂ (NCS) ₂	Co(py) ₂ (NCS) ₂	Fe(py) ₄ (NCS) ₂
7.33 vs	7.33 vs	8.11 vs
		7.05 w
		6.70 w
5.24 m	5.24 m	4.41 m
5.11 m	5.11 m	4.31 w
		4.09 w
		4.00 w
4.25 m	4.25 m	3.88 m
		3.82 m
		3.56 s
		2.96 s
		2.86 s
2.84 w	2.84 s	
2.76 w	2.76 w	2.68 w
2.64 w	2.64 m	2.49 w
2.43 w	2.43 w	2.39 w
2.38 w	2.38 w	
2.36 w	2.36 w	
2.25 w	2.25 w	
2.24 w	2.24 w	
		2.21 w
		2.19 w
		2.07 w
1.85 w	1.85 w	
1.84 w	1.84 w	
1.80 w	1.80 w	

^a Values are *d* spacings in angstroms. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

Table II. Magnetic Susceptibility Data

Compd	T, °K	10 ⁶ χ _M ['] , cgsu	μ _{eff} , BM
Fe(py) ₂ (NCS) ₂	117.0	32,210	5.49
Mol wt 330.21	147.5	25,360	5.47
χ _M ^c = 181 cgsu	193.0	19,480	5.48
	227.0	16,470	5.47
	295.5	12,620	5.46
Fe(py) ₄ (NCS) ₂	120.5	30,960	5.46
Mol wt 488.4	145.5	25,450	5.44
χ _M ^c = 274 cgsu	150.5	24,600	5.44
	199.0	18,710	5.46
	248.0	14,960	5.45
	294.0	12,670	5.46

cantly lower than the value reported by Gill and Nyholm.²³ The magnetic moments are essentially independent of temperature between 120°K and room temperature. The magnitude and temperature independence of the moments are reasonable for tetragonally distorted, octahedral, high-spin iron(II) complexes.²⁴ No attempt has been made to evaluate the magnitude of the distortion from octahedral symmetry because lower temperature susceptibility data are not available.²⁵

The infrared spectral results and band assignments for Fe(py)₂(NCS)₂ and Fe(py)₄(NCS)₂ are presented in Table III. The spectra of the two compounds are similar except for several notable bands, the presence of which may be understood in terms of the structural differences in the two com-

Table III. Infrared Spectral Results

Fe(py) ₂ (NCS) ₂	Fe(py) ₄ (NCS) ₂	Assignment
2150 sh	2090 sh	ν(N-CS)
2090 vs	2065 vs	
2050 sh	2017 sh	
783 w	807 m	ν(NC-S)
634 s	623 s	ν(pyridine ring)
473 m	481 m	δ(NCS)
261 s	267 s	ν(Fe-NCS)
208 s	200 s	ν(Fe-Npy)
185 s		ν(Fe-SCN)
163 s	165 s	?

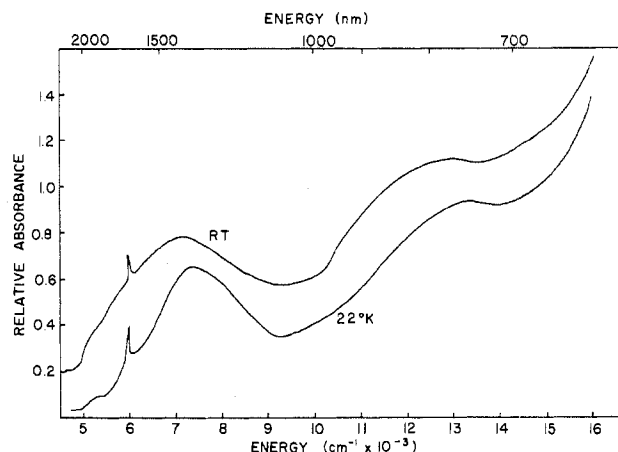


Figure 1. The electronic absorption spectrum of Fe(py)₂(NCS)₂ at room temperature and 22°K.

pounds. The infrared vibrational properties of the thiocyanate ligand have been extensively studied as a function of its mode of coordination and the resulting structure of the complex. Chatt and Duncanson²⁶ concluded that infrared bands were valuable in distinguishing between terminal or bridging thiocyanate coordination. Forster and Goodgame³ studied the infrared spectra of bridging thiocyanate ligands in the 200- to 400-cm⁻¹ region and concluded that the metal-sulfur stretching band must occur below 200 cm⁻¹. At about the same time, Clark and Williams²⁷ studied the stereochemistry of the metal pyridine complexes and found that the pyridine ring vibration at 604 cm⁻¹ is very sensitive to the stereochemistry of the complex. Their results indicate that, in a monomeric octahedral iron(II) complex, this band is located at about 620 cm⁻¹, whereas, in a polymeric octahedral iron(II) complex, the band is 10 to 15 cm⁻¹ higher in energy. In the polymeric octahedral complex, Fe(py)₂(NCS)₂, this pyridine ring vibration is assigned to a band at 634 cm⁻¹, whereas in the octahedral Fe(py)₄(NCS)₂ complex the related band is found at 623 cm⁻¹. This condition of course is consistent with the above cited prediction²⁷ and with the work of several other authors.^{2,28,29} It should be noted that both ν(NC-S) and δ(NCS) are found at higher energies in the tetrakis than in the bis complex; however, the energy difference is much smaller than that found for terminal nitrogen and terminal sulfur bonded thiocyanate ligands.³⁰ This smaller difference can be understood on the basis of the slightly smaller

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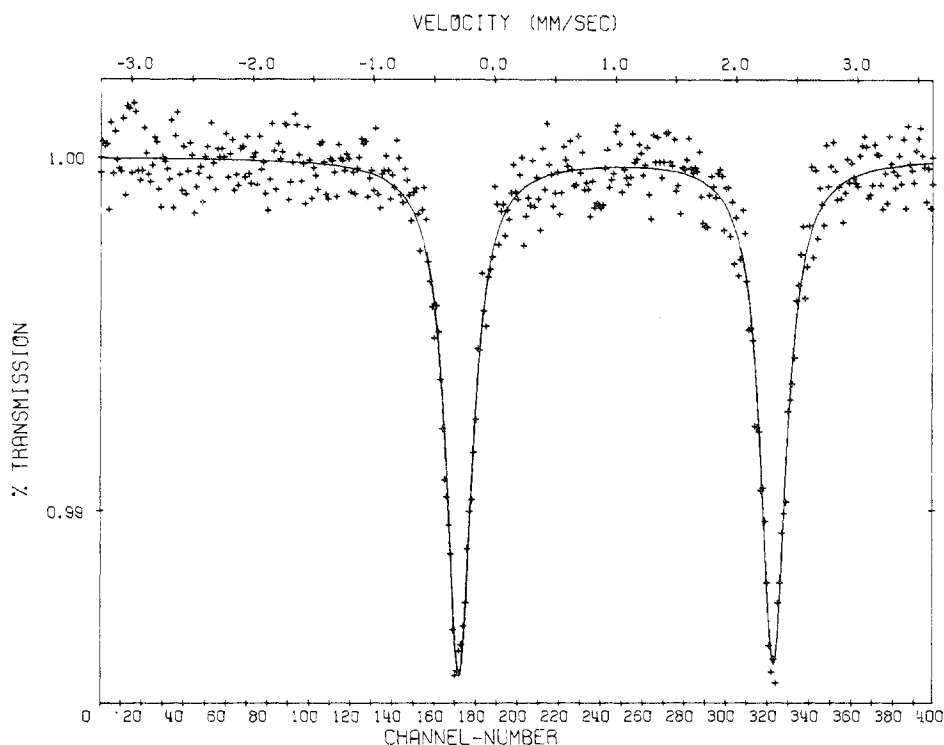


Figure 2. Mössbauer spectrum of $\text{Fe}(\text{py})_2(\text{NCS})_2$ at room temperature.

carbon-sulfur bond order in the bridging ligand as compared with the terminal nitrogen-bonded thiocyanate. The difference in the carbon-sulfur bond order is, of course, larger for the two possible terminal bonded ligands.²⁸ The band at 185 cm^{-1} in $\text{Fe}(\text{py})_2(\text{NCS})_2$ has been assigned to the iron-sulfur stretching vibration; no similar band is observed in $\text{Fe}(\text{py})_4(\text{NCS})_2$. The assignments of the $\nu(\text{N-CS})$ and $\delta(\text{NCS})$ bands are in excellent agreement with the previous work of Clark and Williams² and with related work by König, *et al.*,³¹ and Nelson and Rodgers.³² It is tempting to assign the band at 163 cm^{-1} in $\text{Fe}(\text{py})_2(\text{NCS})_2$ to a bending vibration associated with the Fe-NCS-Fe group;³³ however, this assignment would be unlikely in view of the similar band at 165 cm^{-1} in the monomeric $\text{Fe}(\text{py})_4(\text{NCS})_2$ complex.

The electronic absorption spectrum of $\text{Fe}(\text{py})_2(\text{NCS})_2$ at 22°K and at ambient temperature is shown in Figure 1. The electronic spectrum of $\text{Fe}(\text{py})_4(\text{NCS})_2$ has been reported previously by several authors,^{7,9,34} and we obtain results which are in substantial agreement with the previous work. The tetrakis complex exhibits a broad partially resolved band extending from *ca.* 8000 to $13,000\text{ cm}^{-1}$ which can be assigned to the partially resolved transitions from the ground state to the ${}^5\text{A}_{1g}$ state (*ca.* $10,000\text{ cm}^{-1}$) and to the ${}^5\text{B}_{1g}$ state (*ca.* $11,500\text{ cm}^{-1}$), which result from the ${}^5\text{B}_g$ excited state in the presence of the tetragonal ligand field. It is apparent that in the tetrakis complex the ${}^5\text{E}_g$ excited state splitting is of the order of 1500 to 2000 cm^{-1} . In contrast, the spectrum of $\text{Fe}(\text{py})_2(\text{NCS})_2$ exhibits two well separated bands at 7200 and $13,100\text{ cm}^{-1}$ at room temperature and at 7400 and $13,300\text{ cm}^{-1}$ at 22°K . On the basis

of the Mössbauer spectral results, presented below, which show that the d_{xy} orbital is the ground state orbital, we assign the 7200-cm^{-1} band to the transition from the ${}^5\text{B}_{2g}$ state that arises from the ${}^5\text{T}_{2g}$ state in O_h symmetry to the ${}^5\text{B}_{1g}$ state that arises from the ${}^5\text{E}_g$ state in O_h symmetry, and we assign the $13,100\text{-cm}^{-1}$ band to the related transition to the ${}^5\text{A}_{1g}$ state. For this compound, the low-symmetry splitting of the ${}^5\text{E}_g$ excited state is *ca.* 6000 cm^{-1} and is independent of temperature. This result indicates a much more highly distorted ligand field in the bis complex than in the tetrakis complex. This situation is certainly consistent with the structures of these two complexes. The bonded sulfur atoms in the bis complex are expected to provide a substantially smaller crystal field than the four coordinated nitrogen atoms about the iron(II) ion. The distortion is, as a result, greater than in the tetrakis complex where six nitrogen atoms make up the coordination sphere. This greater distortion is also clearly observed in the Mössbauer spectra of the two compounds. The small increase in the energy of the electronic transitions with decreasing temperature is most likely a result of an increase in the ligand field strength with decreasing temperature which arises from a slight contraction of the unit cell volume at low temperature.

The electronic spectrum of $\text{Fe}(\text{py})_2(\text{NCS})_2$ exhibits a strong and broad band at $21,700\text{ cm}^{-1}$ which is very similar to the intense band found³⁴ at $19,000\text{ cm}^{-1}$ in the so called "black" isomer of $\text{Fe}(\text{py})_4(\text{NCS})_2$. This band is no doubt due to a small amount of iron(III) impurity, which, in the presence of the thiocyanate ligand, exhibits a strong high-intensity charge transfer band at about $20,000\text{ cm}^{-1}$. In $\text{Fe}(\text{NCS})_6^{3-}$, this band is found³⁵ at *ca.* $21,400\text{ cm}^{-1}$. The amount of iron(III) impurity must be quite small, because it is not observed in any of the other physical properties of the compound.

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Table IV. Mossbauer Spectral Parameters

	T , °K	δ , ^a mm/sec	ΔE_Q , mm/sec	Γ_1 , ^b mm/sec	Γ_2 , ^b mm/sec
Fe(py) ₂ (NCS) ₂	78	1.13	3.03	0.29	0.32
	RT	1.00	2.61	0.26	0.26
Fe(py) ₄ (NCS) ₂	78	1.17	2.00	0.26	0.26
	RT	1.05	1.54	0.25	0.24

^a Relative to natural iron foil. ^b Full width at half-maximum for low-velocity line Γ_1 , and high-velocity line Γ_2 .

The unperturbed Mossbauer spectrum of Fe(py)₂(NCS)₂ at room temperature is presented in Figure 2. The Mossbauer spectral parameters for both the bis and tetrakis complexes are presented in Table IV. The results for Fe(py)₄(NCS)₂ are in excellent agreement with the results of previous reports.^{4,5,22} The Mossbauer results for Fe(py)₂(NCS)₂ also agree well with the work of Tominaga, *et al.*,⁵ who have studied the thermal decomposition of Fe(py)₄(NCS)₂. The larger distortion of the crystal field in the bis complex relative to the tetrakis complex can result in a larger electric field gradient. This is observed in the significantly larger quadrupole splitting exhibited by Fe(py)₂(NCS)₂. This difference as mentioned previously may be a direct result of the different atoms which comprise the coordination sphere of the two compounds. It is interesting to note, however, that the temperature dependence of the quadrupole splitting is large and of the same order of magnitude (*ca.* 0.4 mm/sec) in both the bis and tetrakis complexes. This temperature dependence⁴ is an indication of an electric field gradient which is a thermal average of the gradients resulting from the occupation of two or more orbital states. Then, as a consequence, the similar temperature dependence of ΔE_Q may indicate a comparable splitting of the ground state t_{2g} orbitals in the two complexes. If this is the case, the difference in magnitude of the quadrupole splitting could be explained on the basis of differing signs for the valence and ligand (or crystal) field contributions to the gradients experienced by the iron(II) nuclei in the two complexes. The small reduction in the chemical isomer shift in the bis complex as compared with the tetrakis complex can be explained by the lower total electronegativity of the coordinated atoms in the bis complex. The lower sulfur electronegativity results in a higher s electron density in the vicinity of the iron nucleus in the bis complex and, consequently, in a smaller chemical isomer shift in Fe(py)₂(NCS)₂.

In order to correctly simulate the low-temperature magnetic Mossbauer spectra, it is necessary to know the sign of the quadrupole interaction. This can be obtained for a polycrystalline sample by using the magnetic perturbation technique.^{36,37} Because Fe(py)₂(NCS)₂ is ordered at 4.2°K, the perturbed experiment was performed at ambient temperatures at which this complex is a simple, rapidly relaxing paramagnet. The results of this experiment are shown in Figure 3 where it can be seen that a triplet occurs at a negative velocity relative to the doublet, which is at the more positive velocity. This occurrence implies a positive, principal component, V_{zz} , of the electric field gradient tensor, and, because the quadrupole moment of the ⁵⁷Fe excited nuclear state is positive, the foregoing result also indicates a positive quadrupole interaction. The latter is consistent with a ⁵B ground state corresponding to an electron in the d_{xy} orbital. The spectrum presented in Figure 3 can be fit

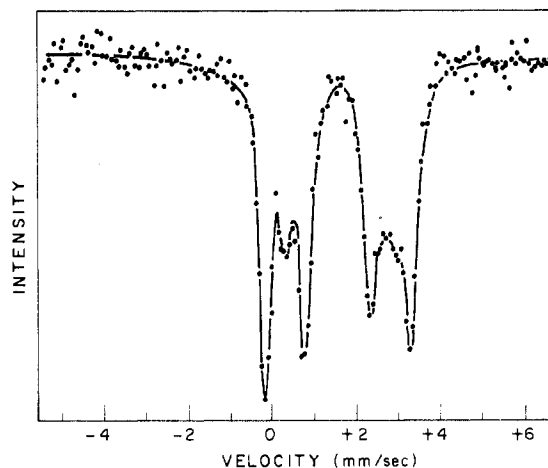


Figure 3. The Mossbauer spectrum of Fe(py)₂(NCS)₂ at room temperature with $H_{\text{longitudinal}} = 45$ kG.

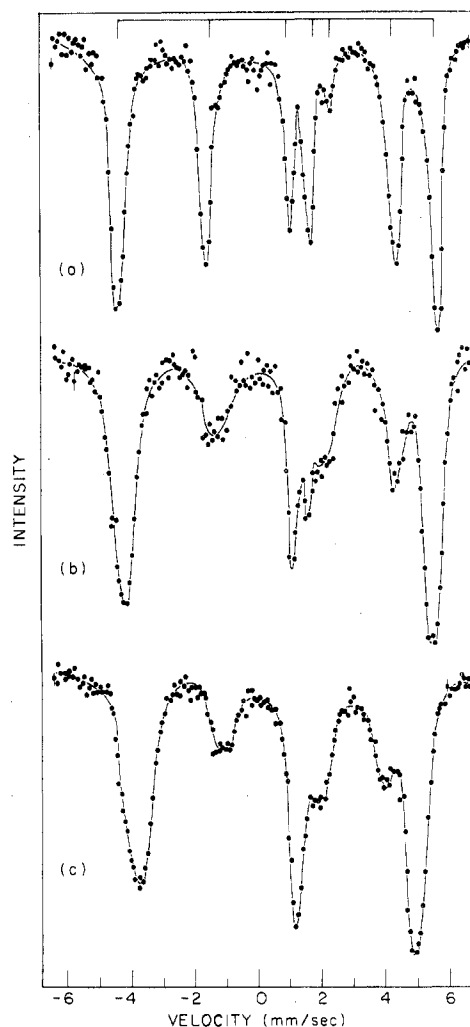


Figure 4. The Mossbauer spectrum of Fe(py)₂(NCS)₂ at 4.2°K with (a) $H_{\text{ext}} = 0$; (b) $H_{\text{longitudinal}} = 40$ kG; and (c) $H_{\text{longitudinal}} = 80$ kG. The solid line is a computer simulation for $H_{\text{hf}} = 280$ kG, $V_{zz} > 0$, $\eta = 0$, and $\beta = 75^\circ$.

reasonably with small values of the asymmetry parameter, η (up to values of *ca.* 0.4). This is consistent with the approximate D_{2h} symmetry of the compound and corresponds to the coordination geometry discussed above.

The Mossbauer spectrum of polycrystalline Fe(py)₂(NCS)₂

(36) W. M. Reiff, *Coord. Chem. Rev.*, **10**, 37 (1973).

(37) R. L. Collins, *J. Chem. Phys.*, **42**, 1072 (1965).

at 4.2°K shows a large magnetic hyperfine splitting (Figure 4a), which indicates that the material is magnetically ordered at this temperature. The spectrum was compared with a computer-simulated spectrum obtained by using the program of Singh and Hoy³⁸ to determine the magnitude of the quadrupole splitting and the value of the angle β between V_{zz} and the hyperfine field, H_{hf} . The magnitude of H_{hf} is 280 kG and was obtained from the ground state splitting observed in the experimental spectrum. An acceptable fit is obtained with $\Delta E_Q = +2.8$ mm/sec, $\beta = 75^\circ$, and $\eta = 0$ and is shown as the bar diagram in Figure 4a. A good fit could not be obtained for $\Delta E_Q = 3.03$ mm/sec. This may indicate that there is a decrease in ΔE_Q with decreasing temperature below 78°K. Confirmation of this decrease will have to await further study. By assuming that the principal axis, V_{zz} , coincides with that of the trans pyridine nitrogen atoms, one can note that a value of β of 75° indicates spin alignment close to the plane determined by the bridging thiocyanate moiety. The effect of external magnetic fields, H_0 , of 40 and 80 kG applied longitudinally is shown in Figures 4b and 4c, respectively. As H_0 increases, the intensity of the $\Delta m = 0$ lines decreases and the overall splitting decreases while the apparent line width increases. These results indicate that, at *these fields*, the material is ferromagnetic but highly anisotropic so that, even at 80 kG, the moments are not completely aligned. Moreover, the sign of the hyperfine field is negative.

If the material were simply a slowly relaxing paramagnet with a small (compared to the Zeeman energy) electronic zero-field splitting, rather than a ferromagnetic, one would expect ready alignment of the spin moments along the field direction and that the intensity of the $\Delta m = 0$ lines would go to zero at smaller applied fields. For an antiferromagnet, the application of an external magnetic field to a polycrystalline sample would result in a broadening of all of the lines but no shift of any line and no diminution of the $\Delta m = 0$ transitions. This condition results because the applied field simply adds vectorially to a random distribution of in-

ternal hyperfine field directions in an isotropic powder. If the electronic zero-field splitting was comparable to the Zeeman splitting, then the "paramagnetic moment" would be difficult to polarize. However, magnetic susceptibility studies to be published³⁹ show that the system is not paramagnetic at 4.2°K.

By analogy to $\text{Fe}(\text{py})_2\text{Cl}_2$, the thiocyanate complex probably orders near 10°K; however, very low temperature susceptibility studies, field dependence of magnetization studies, and Mossbauer spectral studies are in progress in an effort to determine T_c precisely and to understand more completely the nature of the magnetic exchange in $\text{Fe}(\text{py})_2(\text{NCS})_2$. With similar bridging geometries in these two complexes, *i.e.*, metal-bridging group-metal angles of *ca.* 90–100°, one would expect the three-atom-bridged system to exhibit a somewhat lower T_c and a weaker exchange interaction than the chloro-bridged system. To conclude, it is worthwhile to point out that preliminary low-temperature magnetization and susceptibility studies on $\text{Fe}(\text{py})_2\text{Cl}_2$ are consistent with previous¹⁰ suggestions of ferromagnetic behavior and will be published subsequently. In addition, we find that both $\text{Fe}(\text{py})_2\text{Cl}_2$ and $\text{Fe}(\text{py})_2(\text{NCS})_2$ exhibit very low-field (*ca.* 1000 G) metamagnetic behavior as discussed in the Introduction.³⁹

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Registry No. $\text{Fe}(\text{py})_2(\text{NCS})_2$, 51652-62-1; $\text{Co}(\text{py})_2(\text{NCS})_2$, 26297-43-8; $\text{Fe}(\text{py})_4(\text{NCS})_2$, 15225-68-0.

(39) W. M. Reiff, S. Foner, R. B. Frankel, B. F. Little, and G. J. Long, *Inorg. Chem.*, in preparation for publication.

(38) K. P. Singh and G. R. Hoy, Boston University, private communication.