a metastable ion at m/e 98.5 ($121^2/148 = 98.9$). The presence of the ion bearing a hydrogen isocyanide ligand has been noted in the spectra of $C_5H_5Mn(CO)_2(CNC_6H_{11})$[36] and $C_5H_5Fe(CO)(NCCF_3)[C(CF_3)=NH]$.[37] π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_2Ph$ breaks down *via* two different pathways. In the first pathway the loss of a benzyl group occurs to afford $C_5H_5Fe(CO)_2[CNC(CH_3)_3]^+$ (m/e 260, ri 42). This ion loses two carbonyls and $CH_2=C(CH_3)_2$ stepwise to $C_5H_5Fe(CHN)^+$ (m/e 148, ri 37). The second pathway is of particular interest. A salient feature of this process involves the simultaneous loss of two carbonyl groups, although losses of two carbonyl groups occur stepwise in the mass spectra of the other acyl isocyanide complexes, π-$C_5H_5Fe(CO)(CNR')COR$, prepared here.

Thus the loss of 2 CO from the parent ion occurs, affording $C_5H_5Fe[CNC(CH_3)_3]CH_2Ph$ (m/e 295, ri 7). This transition is confirmed by the observation of a metastable ion at m/e 247.5 ($295^2/351 = 247.9$) and the high-resolution mass spectrum of this complex.[38] Some examples of the simultaneous loss of carbonyl groups have been noted in the mass spectra of several arenemetal complexes.[33,34] The successive losses of the $CH_2=C(CH_3)_2$ and HNC groups occur from the ion (m/e 295), finally giving the iron ion.

(b) π-$C_5H_5Fe(CO)_2[C(R)=NR']$. Many examples of decarbonylation of metal carbonyl derivatives, resulting in the absence of the parent peak in the mass spectrometer have been noted.[39-41] An example among such compounds is observed in the mass spectra of the iminoacyl complexes.

In the spectrum of π-$C_5H_5Fe(CO)_2[C(CH_2Ph)=NC_6H_{11}]$, the loss of CO from the highest ion $C_5H_5Fe(CO)[C(CH_2Ph)=NC_6H_{11}]^+$ (m/e 349, ri 22) occurs to give $C_5H_5Fe[C(CH_2Ph)=NC_6H_{11}]^+$ (m/e 321, ri 75). This ion appears to break down *via* two pathways. In the first the successive losses of C_6H_{11} and CN occur to form $C_5H_5FeCH_2Ph^+$ (m/e 212, ri 100). This loses the $PhCH_2$ and C_5H_5 groups to give Fe^+. In the second the loss of $PhCH_2$ occurs, affording $C_5H_5Fe(CNC_6H_{11})^+$ (m/e 230, ri 66). The mass spectrum of π-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4Cl\text{-}p)=NC_6H_{11}]$ gives a fragmentation pattern similar to that of the benzyl derivative.

In the spectrum of π-$C_5H_5Fe(CO)_2[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]$ the second path leading to formation of the ion $C_5H_5Fe(CNC_6H_{11})^+$ from $C_5H_5Fe[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]^+$ (m/e 341, ri 35) is not detectable. The successive losses of CO, C_6H_{11}, and CN from the highest ion $C_5H_5Fe(CO)[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]^+$ (m/e 369, ri 58) occur to form $C_5H_5FeC_6H_4Cl\text{-}p^+$ (m/e 232, ri 19).

Registry No. $[\pi\text{-}C_5H_5Fe(CO)\{CNC(CH_3)_3\}]_2$, 51567-87-4; π-$C_5H_5Fe(CO)(CNC_6H_{11})I$, 36644-63-0; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]I$, 51567-85-2; π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$, 51567-70-5; π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2C_6H_4Cl\text{-}p$, 51567-76-1; π-$C_5H_5Fe(CO)(CNCH_2Ph)CH_2C_6H_4Cl\text{-}p$, 51567-77-2; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_2Ph$, 51567-72-7; π-$C_5H_5Fe(CO)_2[C(CH_2Ph)=NC_6H_{11}]$, 51567-81-8; π-$C_5H_5Fe(CO)_2[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]$, 51567-80-7; π-$C_5H_5Fe(CO)(CNC_6H_{11})Cl$, 51567-74-9; π-$C_5H_5Fe(CO)(CNCH_2Ph)I$, 51567-84-1; π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_2Ph$, 51567-73-8; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COPh$, 51567-71-6; π-$C_5H_5Fe(CO)(CNC_6H_{11})COC_6H_4Cl\text{-}p$, 51567-75-0; π-$C_5H_5Fe(CO)(CNC_6H_{11})COC_3H_7\text{-}i$, 51567-78-3; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COC_3H_7\text{-}i$, 51567-79-4; π-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4Cl\text{-}p)=NC_6H_{11}]$, 51567-83-0; π-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4Cl\text{-}p)=NCH_2Ph]$, 51567-82-9; $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, 12154-95-9; π-$C_5H_5Fe(CO)_2I$, 12078-28-3; $PhCH_2MgCl$, 6921-34-2; CO, 630-08-0.

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(38) The metastable ion at m/e 247.5 corresponds to the 2 CO or the $CH_2=C(CH_3)_2$ fragment. The exact mass of m/e 295 was counted as m/e 295.098, identical with that of the ion $C_5H_5Fe[CNC(CH_3)_3]CH_2Ph^+$ (m/e 295.102). For comparison the exact mass of the ion $C_5H_5Fe(CO)_2(CNH)CH_2Ph^+$ is m/e 295.030.

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Nature of the Electronic Ground State in Tris(2-chlorophenanthroline)iron(II) Perchlorate and Related Complexes

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The orbital and spin ground states of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ (phen = phenanthroline) and related high-spin ferrous complexes have been studied using Mossbauer spectroscopy. The temperature dependence of the Mossbauer spectrum of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ over the range 300–4.2°K indicates the system to have a ground *spin quintet* contrary to the results of a recent susceptibility study in which a high-spin to low-spin equilibrium is assumed. Magnetically perturbed Mossbauer spectra of the 2-Cl complex as well as the high-spin form of $[Fe(phen)_2(NCS)_2]$ show these compounds to have a *negative* principal component (V_{zz}) of the electric field gradient tensor. This result is consistent with previous Mossbauer and magnetic studies of $[Fe(phen)_2X_2]$ complexes ($X^- = Cl^-, N_3^-$) and is interpreted in terms of an electron in d_{z^2} corresponding to an *orbital* (^2A) *singlet* ground term.

The purpose of this work is the elucidation of both the orbital and spin ground states of certain high-spin ferrous (diimine) complexes which have been the subject of several recent studies.

Spin Ground State

Extensive data[1] exist establishing that nearly all six-coordinate iron(II) complexes of the type $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ have diamagnetic (^1A) ground states. This same

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generalization also applies to a wide variety of analogous substituted diimine complexes where both the type of substituent and its position of substitution on the diimine ring may be varied. However, two notable exceptions occur when the diimine ligand is either 2-methylphenanthroline or 2-chlorophenanthroline. The first of these ligands has recently been shown[2,3] to form tris iron(II) complexes with ground states near the "spin-crossover point" such that spin quintet properties are observed for the complexes at room temperature and spin singlet properties are observed at lower temperatures. Over the temperature range of 300-77°K, the effective magnetic moments of these compounds decrease by *ca.* 2 BM to values of *ca.* 3 BM and two species characteristic of high-spin and low-spin iron(II) are observed in the Mossbauer spectra of the compounds. In another recent investigation, Halbert, *et al.*,[4] attributed similar spin-state behavior to the $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ complex on the basis of a decrease in μ_{eff} from 5.4 BM at 300°K to 5.0 BM at 100°K. In this article we present Mossbauer spectral data at variance with the foregoing assignment of spin-state equilibrium behavior to this 2-chlorophenanthroline complex. We also present magnetically perturbed Mossbauer spectra for this complex and for the related high-spin form of $Fe(phen)_2(NCS)_2$. These perturbed spectra provide useful information on the orbital ground states found in this type of complex.

The magnetically unperturbed Mossbauer spectrum of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ at 4.2°K is presented in Figure 1A and the pertinent Mossbauer parameters measured at several temperatures are presented in Table I. These results indicate that, over the temperature range studied, there is only high-spin iron(II) present in $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$; there is no evidence for a low-spin form of this complex even at 4.2°K. For the low-spin form of the complex, one would expect to observe a doublet with a small quadrupole splitting (*ca.* 0.5 mm/sec) and a small isomer shift (*ca.* 0.2-0.4 mm/sec). These values are typical of those observed for many low-spin tris-diimine complexes and are similar to those reported[3] for the low-spin form of $[Fe(2\text{-}Me(phen))_3](ClO_4)_2$. The magnitude and temperature dependence of the Mossbauer parameters for the 2-chlorophenanthroline complex are quite similar to those observed[3] for the high-spin form of the 2-methylphenanthroline complex and are characteristic of the high-spin quintet ground state over the entire temperature range.

In order to ensure that our sample of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ was the same as that studied by Halbert, *et al.*,[4] we have measured and confirmed some of their previously reported physical properties. For a sample which gave the proper analysis for the above formulation, we observe essentially the same decrease in the effective magnetic moment (0.42 BM over the temperature range of 295.5-113.5°K) as reported previously. In addition, our sample has the same color (orange-yellow) and exhibits the same broad electronic absorption band centered at *ca.* 11,000 cm^{-1}. This band corresponds to the $^5T_{2g}$ to ^5E_g transition described earlier.[4]

A theoretical analysis[3] of the magnetic data for $[Fe(2\text{-}Me(phen))_3](ClO_4)_2$ required a temperature-dependent energy separation between the $^5T_{2g}$ and $^1A_{1g}$ electronic states, with the separation increasing from 300 cm^{-1} at 294°K to 990 cm^{-1} at 98°K. A similar analysis[4] of the magnetic properties of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ led to an energy separation of only 80 cm^{-1}. In spite of this presumed small energy separation, no low-spin form of the complex is observed even at 4.2°K. This result would appear to indicate that the complex is fully high spin at all temperatures and does not possess a ligand field which is near the spin-crossover point. Although the steric effects for both the 2-chloro and 2-methyl substituents are no doubt comparable, the basicity of the 2-chlorophenanthroline ligand[5] is reduced somewhat by the electron-withdrawing ability of the chlorine atom ortho to the chelating nitrogen atom.

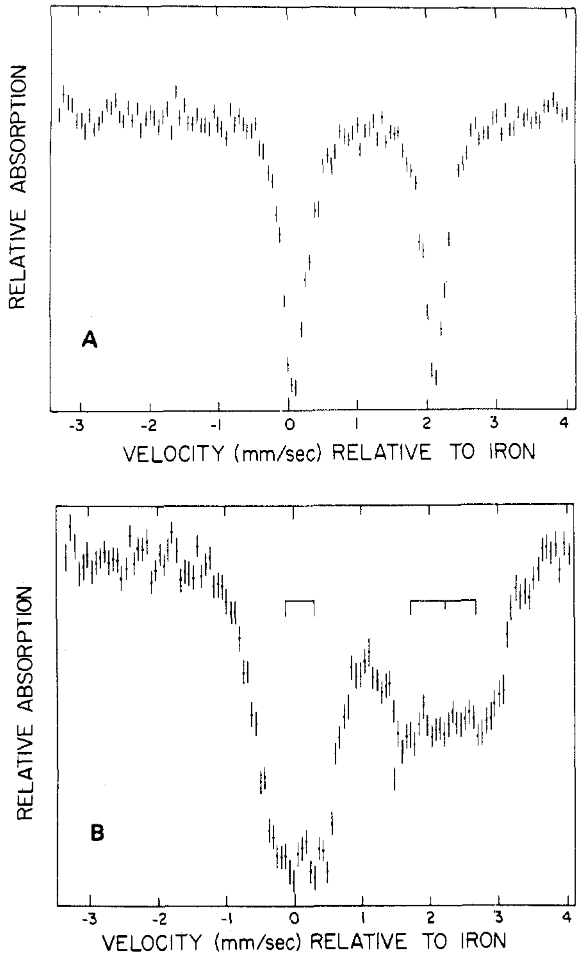

Figure 1. Mossbauer spectrum of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ at 4.2°K and (A) $H_{\text{ext}} = 0$ and (B) $H_{\text{longitudinal}} = 70$ kG.

Table I. Mossbauer Spectra Parameters for $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$

T, °K	δ,[a] mm/sec	ΔE_Q, mm/sec
300	0.99	1.30
78	1.09	2.03[b]
4.2[c]	1.01	1.93

[a] Relative to α-iron. [b] This value differs significantly from the previous value reported by Collins, *et al.*[1] It is believed that in ref 1, low-temperature (78°K) equilibrium with the sample was not achieved.[d] This is strongly suggested by the fact that the high- to low-spin transition of $Fe(phen)_2(NCS)_2$ was not observed in ref 1 while several other workers[d] have clearly demonstrated this transition using Mossbauer spectroscopy. [c] Both source and absorber at 4.2°K. [d] E. Konig, K. Madeja, and K. J. Watson, *J. Amer. Chem. Soc.*, 90, 1146 (1968).

It might finally be argued that an electron interconversion between the presumed high-spin and low-spin forms of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ is occurring on a time scale that is ra-

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pid relative to the lifetime of the excited ($I = {}^{3}/_{2}$, 14.4 keV) state of the iron-57 nucleus and as a result only one species is observed in the Mossbauer spectra measured at various temperatures. This explanation has been used to understand the temperature dependence observed in the Mossbauer spectra of several iron(III) complexes such as tris(*N*,*N'*-dialkyldithiocarbamate)iron(III).[6] However, this rapid interconversion between spin states should lead to Mossbauer spectral parameters which reflect an average of the high-spin and low-spin electronic environments. Neither the temperature dependence nor the magnitude of the Mossbauer parameters presented in Table I provides any evidence for the occurrence of such an averaging process.

The authors believe that the temperature dependence of the magnetic moment of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ may better be explained in terms of a low-symmetry component (of *ca.* ±500 cm^{-1}) of the octahedral ligand field, which, when mixed with spin-orbit and covalency effects, lowers μ_{eff} with decreasing temperature. For example, the magnetic moments of $Fe(phen)_2X_2$ (where X is the chloride, bromide, iodide, or azide ion) undergo a small decrease with decreasing temperature, and in most instances, this decrease may be adequately understood in terms of low-symmetry components of the ligand field rather than in terms of a spin-crossover type of behavior.[7] It is evident that when the decrease in μ_{eff} with temperature is small, magnetic measurements at temperatures well below 77°K are required for the verification of the ground spin state.

Orbital Ground State

The nature of the orbital ground state as well as the spin state of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ and related high-spin complexes is also of interest. Information about the nature of the orbital ground state may be obtained by measuring the Mossbauer spectrum of a compound in a large external magnetic field.[8,9] In particular, the sign of the principal component of the electric field gradient tensor (V_{zz}) can often be determined and correlated with one of several alternative ground-state wave functions provided the contribution of the bonding electrons to the electric field gradient is small. Thus for an axial field resulting from a tetragonal ligand symmetry, the quadrupole splitting results primarily from a nonbonding electron in either a d_{xy} orbital (with $V_{zz} > 0$) or in the d_{xz} and d_{yz} orbitals (with $V_{zz} < 0$). For $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ which contains three bidentate ligands, threefold quantization is more appropriate for the description of the reduction of the ligand field from octahedral to, say, D_3 symmetry. With threefold quantization, the trigonal distortion[10] results in either an orbital singlet whose wave function is $t^0{}_{2g} = d_{z^2}$ with $V_{zz} < 0$ or an orbital doublet, $t^{\pm}{}_{2g}$, where

$$t^{+}{}_{2g} = (2/3)^{1/2}\,|d_{x^2-y^2}\rangle - (1/3)^{1/2}\,|d_{xz}\rangle$$

and

$$t^{-}{}_{2g} = (2/3)^{1/2}\,|d_{xy}\rangle + (1/3)^{1/2}\,|d_{yz}\rangle$$

with $V_{zz} > 0$. Thus, although the choice of symmetry axis for the description of the trigonal distortion does not affect the magnitude of the quadrupole interaction, it does reverse the sign of V_{zz} and hence the choice cannot be made arbitrarily. The Mossbauer spectrum of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ obtained at 4.2°K and in a 70-kG longitudinal magnetic field is presented in Figure 1B. The presence in this spectrum of the doublet at negative velocity and the triplet at positive velocity indicates that V_{zz} is negative for this complex. An orbital scheme corresponding to this electric field gradient tensor is presented in the center of Figure 2.

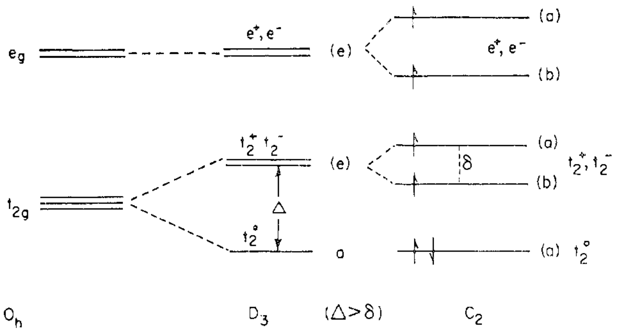

Figure 2. Orbital scheme for high-spin $[Fe(diimine)_3]^{2+}$ and cis$[Fe(diimine)_2X_2]$ complexes.

One can consider even further reduction of the site symmetry for the $[Fe(2\text{-}Cl(phen))_3]^{2+}$ cation than illustrated by the center of Figure 2. Two geometric isomers are possible. These are the meridional (C_1 symmetry) and facial (C_3 symmetry) isomers where the latter is perhaps less stable from the point of view of steric interaction of the three chlorine atoms. In addition the same isomers and symmetries result if one assumes there is a measurable difference in the basicity of the two nitrogen atoms on each phenanthroline ligand for chloro substitution at the two position. The more stable C_1 isomer is expected to correspond to a ground orbital singlet consistent with the results of this investigation.

The foregoing orbital scheme can also be used to explain the large *negative* quadrupole splittings found in $Fe(phen)_2Cl_2$ and $Fe(phen)_2(N_3)_2$ and in the high-spin forms of $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$. There is a good deal of data[11,12] which indicates that the foregoing complexes contain cis rather than trans monodentate ligands. The interpretation of the quadrupole splitting for these compounds has proven difficult in that their large quadrupole splitting values and the temperature dependence of their splittings have been explained[13] on the basis of a d_{xy} ground-state orbital. This ground-state orbital, however, requires a positive V_{zz}. Another approach[14] at reconciling the observed negative sign of V_{zz} with the magnitude of the quadrupole splitting in these complexes has been the use of an orbital ground-state wave function of the form

$$\psi = \alpha\,|d_{xy}\rangle + \beta\,|d_{xz}\rangle + \gamma\,|d_{yz}\rangle$$

a linear combination of the real d orbitals corresponding to fourfold quantization. This approach has been criticized[15] because of its neglect of spin-orbit effects. Based upon a consideration of the symmetry of the complexes involved, it seems that the forementioned approaches fail to use the appropriate orbital basis set. If we envision the formation

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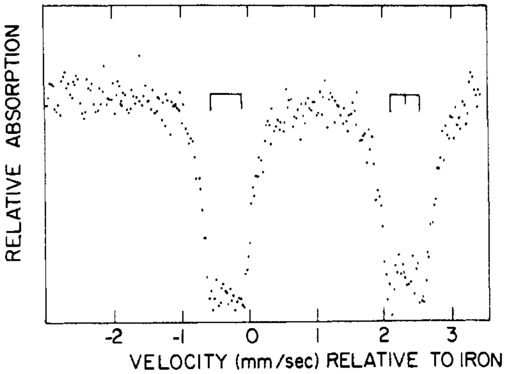

Figure 3. Mossbauer spectrum of Fe(phenanthroline)$_2$(NCS)$_2$ at 300°K and $H_{\text{tranverse}} = 20$ kG.

of Fe(phen)$_2$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 ^{5}A 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 Fe(phen)$_2$(NCS)$_2$ in which the quadrupole splitting at 300°K is found to be −2.67 mm/sec. A similar situation[16] exists for pairs of low-spin iron(III) complexes such as [Fe(phen)$_3$]$^{3+}$ and *cis*-[Fe(phen)$_2$(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 susceptibilities[7] and quadrupole splittings[12] for high-spin Fe(diimine)$_2$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 ^{5}B ground state) and one composed primarily of the d_{z^2} orbital (a ^{5}A ground state).

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Registry No. [Fe(2-Cl(phen))$_3$](ClO$_4$)$_2$, 51829-85-7; Fe(phen)$_2$(NCS)$_2$, 15319-93-4.

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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, Fe(py)$_2$(NCS)$_2$, has been prepared by thermolysis of the tetrakis complex, Fe(py)$_4$(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 Fe(py)$_4$(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 study[10] 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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