

Preparation and Characterization of Bis[2-(2-pyridyl)benzimidazole]iron(II) Complexes

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Bis[2-(2-pyridyl)benzimidazole]iron(II) complexes, $\text{Fe}(\text{PBI})_2\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^- , NCS^- , N_3^- , and CN^-), were prepared and characterized on the basis of their infrared and Mössbauer spectra. In $\text{Fe}(\text{PBI})_2(\text{NCS})_2$, the NCS^- groups are N-bonded. The CN^- groups of $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$ are in a *cis* position. Except for $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$, the Mössbauer parameters are in the range characteristic of a Fe^{2+} ion in a high-spin form. On the other hand, the parameters of $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$ are characteristic of an iron(II) ion in a low-spin form.

INTRODUCTION

Iron(II) octahedral complexes may exist in either one of two different electronic ground states, $^5\text{T}_2$ (high-spin $t_2^4e^2$) and $^1\text{A}_1$ (low-spin t_2^6). If $|d-\pi|$ is smaller than 2000 cm^{-1} , where d represents a ligand-field splitting and π a mean pairing energy of d electrons, an equilibrium between the $^1\text{A}_1$ and $^5\text{T}_2$ states can be expected to occur¹⁾. Certain tris[2-(2-pyridyl)benzimidazole]iron(II) complexes exhibit anomalous magnetic behaviors indicative of the $^5\text{T}_2$ - $^1\text{A}_1$ crossover.^{2,3)}

We have prepared bis[2-(2-pyridyl)benzimidazole]iron(II) complexes $\text{Fe}(\text{PBI})_2\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^- , NCS^- , N_3^- , and CN^-) and characterized on the basis of their infrared and Mössbauer spectra to obtain further features of the iron(II) complexes of 2-(2-pyridyl)benzimidazole.

EXPERIMENTAL

2-(2-Pyridyl)benzimidazole was prepared by using the procedure described previously.³⁾

Preparation of Complexes.

All the preparations were carried out in a nitrogen atmosphere using air-free water, acetone, and 3-methyl-1-butanol. All the complexes were dried *in vacuo* over silica gel at room temperature.

(a) **Dichlorobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, $\text{Fe}(\text{PBI})_2\text{Cl}_2\cdot\text{H}_2\text{O}$:** 2-(2-Pyridyl)benzimidazole dissolved in acetone was added to a ferrous chloride solution prepared by mixing ferrous sulphate heptahydrate and barium chloride dihydrate solutions. When acetone was added to the filtered solution, reddish-brown crystals were precipitated. *Found:* C, 53.60; H, 3.67; N, 15.47%. *Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_6\text{OCl}_2\text{Fe}$:* C, 53.86; H, 3.77; N, 15.71%.

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(b) **Dibromobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, $\text{Fe}(\text{PBI})_2\text{Br}_2\cdot\text{H}_2\text{O}$:** This red complex was prepared as described in (a) by using barium bromide dihydrate instead of barium chloride dihydrate. *Found:* C, 46.43; H, 3.15; N, 13.49%. *Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_6\text{OBr}_2\text{Fe}$:* C, 46.18; H, 3.23; N, 13.47%.

(c) **Dithiocyanatobis[2-(2-pyridyl)benzimidazole]iron(II), $\text{Fe}(\text{PBI})_2(\text{NCS})_2$:** 2-(2-Pyridyl)benzimidazole dissolved in the minimum of acetone was added to a ferrous chloride solution. A concentrated aqueous solution of NaSCN was added to the filtered dark-red solution and the mixture led alone for some time. The reddish-brown crystals thus precipitated were filtered, suspended in 3-methyl-1-butanol and then refluxed for 6 hr.

(d) **Diazidobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, $\text{Fe}_2(\text{PBI})_2(\text{N}_3)_2\cdot\text{H}_2\text{O}$:** A concentrated aqueous solution of NaN_3 was added to a filtered solution of ferrous chloride and 2-(2-pyridyl)benzimidazole. After a while, the deep brown crystals were filtered.

(e) **Dicyanobis[2-(2-pyridyl)benzimidazole]iron(II) Dihydrate, $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$:** A concentrated aqueous solution of NaCN was added to a filtered solution of ferrous chloride and 2-(2-pyridyl)benzimidazole, and the purplish red crystals were filtered and then refluxed for 6 hr in acetone. *Found:* C, 58.09; H, 3.52; N, 20.53; Fe, 10.55%. *Calcd for $\text{C}_{26}\text{H}_{22}\text{N}_8\text{O}_2\text{Fe}$:* C, 58.44; H, 4.15; N, 20.97; Fe, 10.45%.

While the values of elementary analysis of $\text{Fe}(\text{PBI})_2(\text{NCS})_2$ and $\text{Fe}(\text{PBI})_2(\text{N}_3)_2\cdot\text{H}_2\text{O}$ coincided with the calculated ones respectively, the Mössbauer spectra of these complexes show that some of $\text{Fe}(\text{PBI})_2\text{Cl}_2$ is mixed in these samples.

Infrared Spectra.

The infrared spectra were measured in Nujol mull with a Perkin-Elmer 521 spectrophotometer.

Mössbauer Effect Measurements.

The Mössbauer spectra were obtained with a scanning velocity spectrometer in the time mode. The radiation source was ^{57}Co diffused in a copper foil and kept at room temperature during all the measurements. The velocity scale was calibrated with metallic iron, and the velocity was determined to an accuracy of ± 0.06 mm/s.

RESULTS AND DISCUSSION

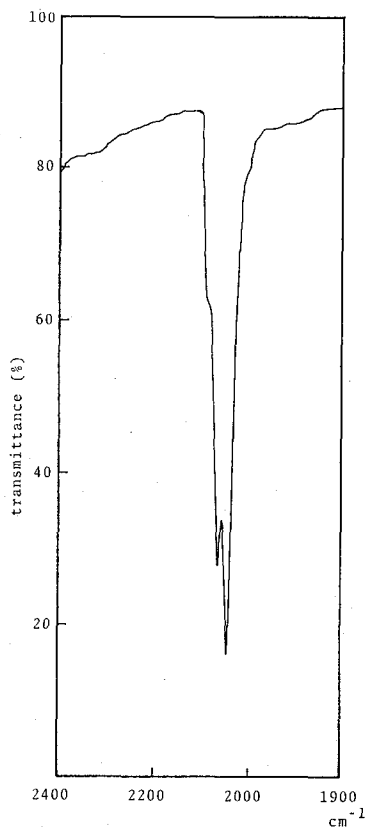
Infrared Spectra.

The infrared frequencies attributed to the vibrations of the X ligands in the $\text{Fe}(\text{PBI})_2\text{X}_2$ complexes ($\text{X}=\text{NCS}^-$, CN^- , and N_3^-) are listed in Table I. The spectrum of $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$ is shown in Fig. 1. Since the absorption bands due to 2-(2-pyridyl)benzimidazole of these complexes change little from $\text{Fe}(\text{PBI})_2\text{Cl}_2\cdot\text{H}_2\text{O}$ and $\text{Fe}(\text{PBI})_2\text{Br}_2\cdot\text{H}_2\text{O}$, it is easy to assign the bands due to the X ligands.

The thiocyanate group is a bifunctional ligand and the fundamental frequencies

Table I. Infrared Frequencies of Ligands X in $\text{Fe}(\text{PBI})_2\text{X}_2$ Complexes (in cm^{-1})

Compound	Frequencies of band maxima		Assignment
$\text{Fe}(\text{PBI})_2(\text{NCS})_2$	2037	2045	C-N stretching
	2079		
$\text{Fe}(\text{PBI})_2(\text{CN})_2 \cdot 2\text{H}_2\text{O}$	2050	2070	C-N stretching
$\text{Fe}(\text{PBI})_2(\text{N}_3)_2 \cdot \text{H}_2\text{O}$	2039	2060	N-N stretching
	2079		

Fig. 1. Infrared spectrum of $\text{Fe}(\text{PBI})_2(\text{CN})_2 \cdot 2\text{H}_2\text{O}$.

based on the C-N stretching vibration depend on whether this group is attached to the metal ion through N or through S. For M-NCS the range appears to be about $2040\text{--}2080\text{ cm}^{-1}$ and for M-SCN about $2080\text{--}2120\text{ cm}^{-1}$.^{4,5)} In $\text{Fe}(\text{PBI})_2(\text{NCS})_2$, the band maxima are observed at 2037, 2045, and 2079 cm^{-1} being in the range characteristic of N-bonded thiocyanate.

Previous investigations have been concentrated on the infrared measurements of C-N frequencies of some mixed cyanide and aromatic diimine complexes of iron.^{6,7)} In the case of $\text{Fe}(\text{phen})_2(\text{CN})_2$ one could expect coupling to split the C-N stretching frequency into two stretching motions. The symmetric stretch would, however, be inactive in the *trans* complex (D_{2h}). A. A. Schilt reported that C-N stretching frequencies of the complex are 2075 and 2062 cm^{-1} in a *cis* form, and 2066 cm^{-1} in

a *trans* form.⁸⁾ In $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$, the C-N stretching shows two peaks at 2070 and 2050 cm^{-1} . While asymmetric 2-(2-pyridyl)benzimidazole leads the complex into a lower symmetry, the C-N stretching mode would be rather sensitive to the position of the cyano ligands. Thus the splitting of the C-N stretching vibration suggests that the cyano groups are in a *cis* position.

Mössbauer Spectra.

The Mössbauer parameters are listed in Table II and the spectra are shown in Fig. 2. All the complexes were measured at *ca.* 110 K.

Table II. Mössbauer Parameters of $\text{Fe}(\text{PBI})_2\text{X}_2$ Complexes

Compound	δ mm/s	ΔE_Q mm/s
$\text{Fe}(\text{PBI})_2\text{Cl}_2\cdot\text{H}_2\text{O}$	1.08	2.63
$\text{Fe}(\text{PBI})_2\text{Br}_2\cdot\text{H}_2\text{O}$	1.06	2.53
$\text{Fe}(\text{PBI})_2(\text{N}_3)_2\cdot\text{H}_2\text{O}$	1.08	2.63
	1.06	2.12
$\text{Fe}(\text{PBI})_2(\text{NCS})_2$	1.08	2.63
	1.08	2.07
$\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$	0.31	0.74

110 K error = ± 0.06 mm/s

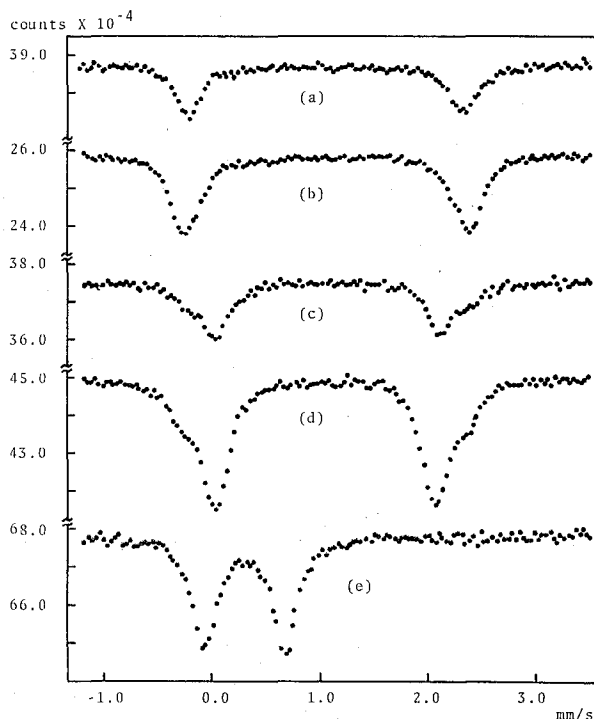


Fig. 2. Mössbauer spectra of $\text{Fe}(\text{PBI})_2\text{X}_2$ complexes at *ca.* 110 K.
 (a) $\text{Fe}(\text{PBI})_2\text{Br}_2\cdot\text{H}_2\text{O}$ (b) $\text{Fe}(\text{PBI})_2\text{Cl}_2\cdot\text{H}_2\text{O}$ (c) $\text{Fe}(\text{PBI})_2(\text{NCS})_2$
 (d) $\text{Fe}(\text{PBI})_2(\text{N}_3)_2\cdot\text{H}_2\text{O}$ (e) $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$

The parameters of $\text{Fe}(\text{PBI})_2\text{X}_2$ ($\text{X}=\text{Cl}^-$, Br^- , NCS^- , and N_3^-) are in the range characteristic of a Fe^{2+} ion in a high-spin form.⁹⁾ The spectra of $\text{Fe}(\text{PBI})_2(\text{NCS})_2$ and $\text{Fe}(\text{PBI})_2(\text{N}_3)_2\cdot\text{H}_2\text{O}$ consist of two doublets. The outer pairs of both complexes center at 1.08 mm/s with a quadrupole splitting of 2.63 mm/s, whose parameters are consistent with the values of $\text{Fe}(\text{PBI})_2\text{Cl}_2\cdot\text{H}_2\text{O}$. Since acetone was used in considerably large quantities to dissolve 2-(2-pyridyl)benzimidazole in the preparation, there is a possibility for $\text{Fe}(\text{PBI})_2\text{Cl}_2$ to be coprecipitated. Thus we conclude that the outer peaks are attributed to $\text{Fe}(\text{PBI})_2\text{Cl}_2$. On the other hand, the parameters of $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$ are characteristic of an iron(II) ion in a low-spin form.

The octahedral complexes of FeA_4B_2 type may exist in either one of two different isomers, *cis* and *trans*. While some correlation between the quadrupole splitting and the geometry in high-spin complexes has not been reported, previous investigations have been intently performed on such a relationship in low-spin compounds.^{10~14)} The calculations according to a point charge model predict that the quadrupole splitting of the *trans*-compounds should be twice that of the *cis*-isomer in magnitude. The relationship has been observed in several series of *cis-trans*-isomers of iron complexes.^{11~13)} But in $\text{Fe}(\text{phen})_2(\text{CN})_2$, the quadrupole splitting of the *cis*-complex is 0.58 mm/s and that of the *trans*-isomer 0.60 mm/s at room temperature.¹¹⁾ The quadrupole splitting of $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$ is 0.74 mm/s in *ca.* 110 K, which is slightly larger than those of *cis*- and *trans*- $\text{Fe}(\text{phen})_2(\text{CN})_2$. Therefore, Mössbauer effect would not be as yet an effective tool to determine the structure of mixed cyanide and α -diimine complexes of iron(II).

The bis[2-(2-pyridyl)benzimidazole]iron(II) complexes, $\text{Fe}(\text{PBI})_2\text{X}_2$, may be classified into three groups on the basis of their magnetic properties: (i) if $\text{X}=\text{Cl}^-$, Br^- , NCS^- , and N_3^- , $\text{Fe}(\text{PBI})_2\text{X}_2$ is a high-spin compound ($^5\text{T}_2$ ground state); (ii) $[\text{Fe}(\text{PBI})_3]^{2+}$ complexes in which $\text{X}_2=2$ -(2-pyridyl)benzimidazole exhibit a spin equilibrium between $^1\text{A}_1$ and $^5\text{T}_2$ states;^{2,3)} (iii) $\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$ is a diamagnetic complex ($^1\text{A}_1$ ground state). The magnetic property of octahedral iron (II) complexes depends on the balance of the crystal-field splitting and the Racah's parameters in magnitude. In the spectrochemical series, the order of the ligands related to this study is $\text{Br}^- < \text{Cl}^- < \text{N}_3^- < -\text{NCS}^- < \text{dipy} \sim \text{phen} < \text{CN}^-$. The classification of the other α -diimine iron(II) complexes on the basis of their magnetic properties, also, shows that there is a similar relationship between the spin state of their complexes and the spectrochemical series of the ligands.^{15~21)} The tris(1,10-phenanthroline)iron(II) and tris(2,2'-bipyridyl)iron(II) complexes are diamagnetic, and $\text{Fe}(\text{phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{bipy})_2(\text{NCS})_2$ have an anomalous magnetic properties due to a $^1\text{A}_1$ and $^5\text{T}_2$ crossover.^{18,19)} Such a change in the spin state for ligand to ligand indicates that 2-(2-pyridyl)benzimidazole gives rise to a weaker ligand-field than do 1,10-phenanthroline and 2,2'-bipyridyl in iron(II) complexes.

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