

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

Tsunenobu SHIGEMATSU\* and Yoshihiro SASAKI\*

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Bis[2-(2-pyridyl)benzimidazole]iron(II) complexes,  $\text{Fe}(\text{PBI})_2\text{X}_2$  ( $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ , and  $\text{CN}^-$ ), were prepared and characterized on the basis of their infrared and Mössbauer spectra. In  $\text{Fe}(\text{PBI})_2(\text{NCS})_2$ , the  $\text{NCS}^-$  groups are N-bonded. The  $\text{CN}^-$  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  $\text{Fe}^{2+}$  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  $2000\text{ cm}^{-1}$ , where  $d$  represents a ligand-field splitting and  $\pi$  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 occur<sup>1)</sup>. 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.<sup>2,3)</sup>

We have prepared bis[2-(2-pyridyl)benzimidazole]iron(II) complexes  $\text{Fe}(\text{PBI})_2\text{X}_2$  ( $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ , and  $\text{CN}^-$ ) 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.<sup>3)</sup>

#### 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%.

\* 重松恒信, 佐々木義弘: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

**(b) Dibromobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate,**

**Fe(PBI)<sub>2</sub>Br<sub>2</sub>H<sub>2</sub>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 C<sub>24</sub>H<sub>20</sub>N<sub>6</sub>OBr<sub>2</sub>Fe: C, 46.18; H, 3.23; N, 13.47%.

**(c) Dithiocyanatobis[2-(2-pyridyl)benzimidazole]iron(II), Fe(PBI)<sub>2</sub>(NCS)<sub>2</sub>:** 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,**

**Fe<sub>2</sub>(PBI)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>H<sub>2</sub>O:** A concentrated aqueous solution of NaN<sub>3</sub> 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,**

**Fe(PBI)<sub>2</sub>(CN)<sub>2</sub>2H<sub>2</sub>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 C<sub>26</sub>H<sub>22</sub>N<sub>8</sub>O<sub>2</sub>Fe: C, 58.44; H, 4.15; N, 20.97; Fe, 10.45%.

While the values of elementary analysis of Fe(PBI)<sub>2</sub>(NCS)<sub>2</sub> and Fe(PBI)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>H<sub>2</sub>O coincided with the calculated ones respectively, the Mössbauer spectra of these complexes show that some of Fe(PBI)<sub>2</sub>Cl<sub>2</sub> 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 <sup>57</sup>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.

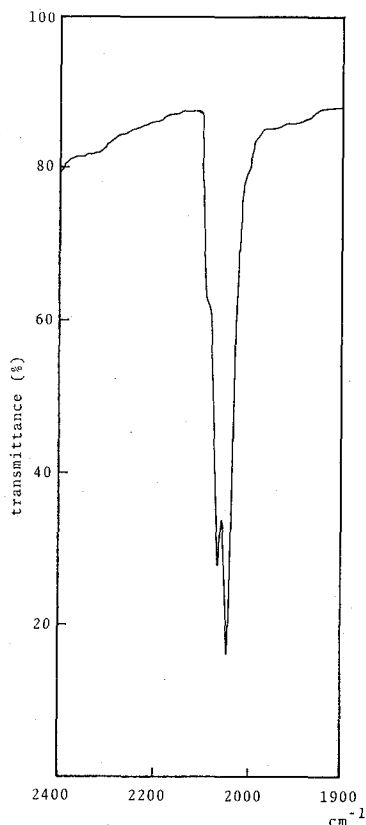
**RESULTS AND DISCUSSION****Infrared Spectra.**

The infrared frequencies attributed to the vibrations of the X ligands in the Fe(PBI)<sub>2</sub>X<sub>2</sub> complexes (X=NCS<sup>-</sup>, CN<sup>-</sup>, and N<sub>3</sub><sup>-</sup>) are listed in Table I. The spectrum of Fe(PBI)<sub>2</sub>(CN)<sub>2</sub>2H<sub>2</sub>O is shown in Fig. 1. Since the absorption bands due to 2-(2-pyridyl)benzimidazole of these complexes change little from Fe(PBI)<sub>2</sub>Cl<sub>2</sub>H<sub>2</sub>O and Fe(PBI)<sub>2</sub>Br<sub>2</sub>H<sub>2</sub>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  $\text{cm}^{-1}$ )

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

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  $2080\text{--}2120\text{ cm}^{-1}$ .<sup>4,5</sup> In  $\text{Fe}(\text{PBI})_2(\text{NCS})_2$ , the band maxima are observed at 2037, 2045, and  $2079\text{ cm}^{-1}$  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.<sup>6,7</sup> 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  $2062\text{ cm}^{-1}$  in a *cis* form, and  $2066\text{ cm}^{-1}$  in

a *trans* form.<sup>8)</sup> 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  $\text{cm}^{-1}$ . 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	$\delta$ mm/s	$\Delta E_Q$ 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 1.06	{ 2.63 2.12
$\text{Fe}(\text{PBI})_2(\text{NCS})_2$	{ 1.08 1.08	{ 2.63 2.07
$\text{Fe}(\text{PBI})_2(\text{CN})_2\cdot 2\text{H}_2\text{O}$	0.31	0.74

110 K error =  $\pm 0.06$  mm/s

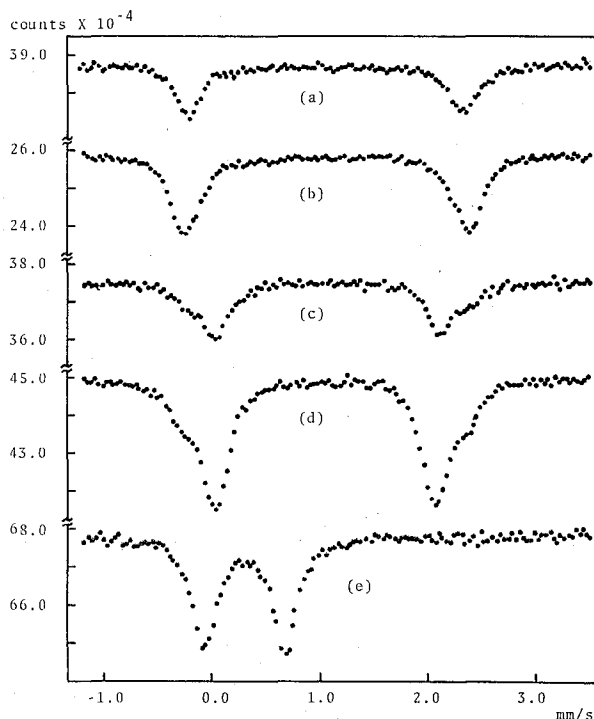


Fig. 2. Mössbauer spectra of  $\text{Fe}(\text{PBI})_2\text{X}_2$  complexes at *ca.* 110 K.  
 (a)  $\text{Fe}(\text{PBI})_2\text{Br}_2\cdot\text{H}_2\text{O}$  (b)  $\text{Fe}(\text{PBI})_2\text{Cl}_2\cdot\text{H}_2\text{O}$  (c)  $\text{Fe}(\text{PBI})_2(\text{NCS})_2$   
 (d)  $\text{Fe}(\text{PBI})_2(\text{N}_3)_2\cdot\text{H}_2\text{O}$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

The parameters of  $\text{Fe}(\text{PBI})_2\text{X}_2$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ , and  $\text{N}_3^-$ ) are in the range characteristic of a  $\text{Fe}^{2+}$  ion in a high-spin form.<sup>9)</sup> The spectra of  $\text{Fe}(\text{PBI})_2(\text{NCS})_2$  and  $\text{Fe}(\text{PBI})_2(\text{N}_3)_2\text{H}_2\text{O}$  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  $\text{Fe}(\text{PBI})_2\text{Cl}_2\text{H}_2\text{O}$ . 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  $\text{Fe}(\text{PBI})_2(\text{CN})_2\text{H}_2\text{O}$  are characteristic of an iron(II) ion in a low-spin form.

The octahedral complexes of  $\text{FeA}_4\text{B}_2$  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 has been intently performed on such a relationship in low-spin compounds.<sup>10~14)</sup> 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.<sup>11~13)</sup> 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.<sup>13)</sup> The quadrupole splitting of  $\text{Fe}(\text{PBI})_2(\text{CN})_2\text{H}_2\text{O}$  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  $\alpha$ -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  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NCS}^-$ , and  $\text{N}_3^-$ ,  $\text{Fe}(\text{PBI})_2\text{X}_2$  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,<sup>2,3)</sup> (iii)  $\text{Fe}(\text{PBI})_2(\text{CN})_2\text{H}_2\text{O}$  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  $\alpha$ -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.<sup>15~21)</sup> 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.<sup>18,19)</sup> 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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