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

Tsunenobu SHIGEMATSU* and Yoshihiro SASAKI*

Received September 30, 1974

Bis[2-(2-pyridyl)benzimidazole]iron(II) complexes, Fe(PBI)$_2$X$_2$ (X=Cl$^-$, Br$^-$, NCS$^-$, N$_3^-$, and CN$^-$), were prepared and characterized on the basis of their infrared and Mössbauer spectra. In Fe(PBI)$_2$(NCS)$_2$, the NCS$^-$ groups are N-bonded. The CN$^-$ groups of Fe(PBI)$_2$(CN)$_2$2H$_2$O are in a cis position. Except for Fe(PBI)$_2$(CN)$_2$2H$_2$O, the Mössbauer parameters are in the range characteristic of a Fe$^{3+}$ ion in a high-spin form. On the other hand, the parameters of Fe(PBI)$_2$(CN)$_2$2H$_2$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, $^3T_2$ (high-spin $t^6_2g^4$) and $^1A_1$ (low-spin $t^6_2g^4$). If $|d-\pi|$ is smaller than 2000 cm$^{-1}$, where $d$ represents a ligand-field splitting and $\pi$ a mean pairing energy of $d$ electrons, an equilibrium between the $^1A_1$ and $^3T_2$ states can be expected to occur\(^1\). Certain tris[2-(2-pyridyl)benzimidazole]iron(II) complexes exhibit anomalous magnetic behaviors indicative of the $^3T_2$-$^1A_1$ crossover.\(^2\,^3\)

We have prepared bis[2-(2-pyridyl)benzimidazole]iron(II) complexes Fe(PBI)$_2$X$_2$ (X=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, Fe(PBI)$_2$Cl$_2$H$_2$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 C$_{24}$H$_{20}$N$_6$OCl$_2$Fe: C, 53.86; H, 3.77; N, 15.71%.

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(b) Dibromobis[2-(2-pyridyl)benzimidazole]iron(II) Monohydrate, Fe(BPI)₂Br₂H₂O: 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 C₂₄H₂₈N₆OBr₂Fe: C, 46.18; H, 3.23; N, 13.47%.

(c) Dithiocyanatobis[2-(2-pyridyl)benzimidazole]iron(II), Fe(PBI)₂(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, Fe₂(PBI)₂(N₃)₂H₂O: A concentrated aqueous solution of NaN₃ 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)₂(CN)₂₂H₂O: 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 C₂₆H₂₂N₈O₂Fe: C, 58.44; H, 4.15; N, 20.97; Fe, 10.45%.

While the values of elementary analysis of Fe(PBI)₂(NCS)₂ and Fe(PBI)₂(N₃)₂H₂O coincided with the calculated ones respectively, the Mössbauer spectra of these complexes show that some of Fe(PBI)₂C₁₂ 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 ⁵⁷Co 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)₂X₂ complexes (X=NCS⁻, CN⁻, and N₇) are listed in Table I. The spectrum of Fe(PBI)₂(CN)₂₂H₂O is shown in Fig. 1. Since the absorption bands due to 2-(2-pyridyl)benzimidazole of these complexes change little from Fe(PBI)₂Cl₂H₂O and Fe(PBI)₂Br₂H₂O, 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 Fe(PBI)$_2$X$_2$ Complexes (in cm$^{-1}$)

<table>
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<tr>
<th>Compound</th>
<th>Frequencies of band maxima</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>Fe(PBI)$_2$(NCS)$_2$</td>
<td>2037 2045 2079</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>Fe(PBI)$_2$(CN)$_2$2H$_2$O</td>
<td>2050 2070</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>Fe(PBI)$_2$(N$_3$)$_2$H$_2$O</td>
<td>2039 2060 2079</td>
<td>N-N stretching</td>
</tr>
</tbody>
</table>

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 2040–2080 cm$^{-1}$ and for M-SCN about 2080–2120 cm$^{-1}$. In Fe(PBI)$_2$(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. In the case of Fe(phen)$_2$(CN)$_2$ one could expected 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
Preparation and Characterization of Iron(II) Complexes of PBI

In Fe(PBI)$_2$(CN)$_2$2H$_2$O, the C-N stretching shows two peaks at 2070 and 2050 cm$^{-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>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ mm/s</th>
<th>$\Delta E_Q$ mm/s</th>
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<tr>
<td>Fe(PBI)$_2$Cl$_2$H$_2$O</td>
<td>1.08</td>
<td>2.63</td>
</tr>
<tr>
<td>Fe(PBI)$_2$Br$_2$H$_2$O</td>
<td>1.06</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe(PBI)$_2$(N$_2$)$_2$H$_2$O</td>
<td>1.08</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>1.06</td>
<td>1.21</td>
</tr>
<tr>
<td>Fe(PBI)$_2$(NCS)$_2$</td>
<td>1.08</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>2.07</td>
</tr>
<tr>
<td>Fe(PBI)$_2$(CN)$_2$2H$_2$O</td>
<td>0.31</td>
<td>0.74</td>
</tr>
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110 K error = ±0.06 mm/s

![Mössbauer spectra of Fe(PBI)$_2$X$_2$ complexes at ca. 110 K.](image)

- (a) Fe(PBI)$_2$Br$_2$H$_2$O
- (b) Fe(PBI)$_2$Cl$_2$H$_2$O
- (c) Fe(PBI)$_2$(NCS)$_2$
- (d) Fe(PBI)$_2$(N$_2$)$_2$H$_2$O
- (e) Fe(PBI)$_2$(CN)$_2$2H$_2$O
The parameters of Fe(PBI)$_2$X$_2$ (X = Cl$^-$, Br$^-$, NCS$^-$, and N$_3^-$) are in the range characteristic of a Fe$^{II}$ ion in a high-spin form. The spectra of Fe(PBI)$_3$(NCS)$_2$ and Fe(PBI)$_3$(N$_3$)$_2$H$_2$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 Fe(PBI)$_2$Cl$_2$H$_2$O. Since acetone was used in considerably large quantities to dissolve 2-(2-pyridyl)benzimidazole in the preparation, there is a possibility for Fe(PBI)$_2$Cl$_2$ to be coprecipitated. Thus we conclude that the outer peaks are attributed to Fe(PBI)$_2$Cl$_2$. On the other hand, the parameters of Fe(PBI)$_2$(CN)$_2$2H$_2$O are characteristic of an iron(II) ion in a low-spin form.

The octahedral complexes of FeA$_4$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. 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. But in Fe(phen)$_2$(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. The quadrupole splitting of Fe(PBI)$_3$(CN)$_2$2H$_2$O is 0.74 mm/s in ca. 110 K, which is slightly larger than those of *cis* - and *trans*-Fe(phen)$_2$(CN)$_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, Fe(PBI)$_2$X$_2$, may be classified into three groups on the basis of their magnetic properties: (i) if X = Cl$^-$, Br$^-$, NCS$^-$, and N$_3^-$, Fe(PBI)$_2$X$_2$ is a high-spin compound ($^3T_2$ ground state); (ii) [Fe(PBI)$_3$]$_2^+$ complexes in which X$_2$ = 2-(2-pyridyl)benzimidazole exhibit a spin equilibrium between $^1A_g$ and $^5T_2$ states; (iii) Fe(PBI)$_2$(CN)$_2$2H$_2$O is a diamagnetic complex ($^1A_g$ 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 Br$^-$ < Cl$^-$ < N$_3^-$ < NCS$^-$ < dipy ~ phen < 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.

The tris(1,10-phenanthroline)iron(II) and tris(2,2'-bipyridyl)iron(II) complexes are diamagnetic, and Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$(NCS)$_2$ have an anomalous magnetic properties due to a $^1A_g$ and $^5T_2$ crossover. 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.

**ACKNOWLEDGMENTS**

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REFERENCES

(18) E. König and K. Madeja, ibid., 6, 48 (1967).