<table>
<thead>
<tr>
<th>Title</th>
<th>Preparation and Characterization of Bis[2-(2-pyridyl)benzimidazole]iron(II) Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Shigematsu, Tsunenobu; Sasaki, Yoshihiro</td>
</tr>
<tr>
<td>Citation</td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1975), 52(5-6): 658-663</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1975-03-31</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/76584">http://hdl.handle.net/2433/76584</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
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$O, the Mössbauer parameters are in the range characteristic of a Fe$^{2+}$ 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, $^5T_2$ (high-spin $t^6_2e^0$) and $^1A_1$ (low-spin $t^6_2$). 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 $^5T_2$ states can be expected to occur. Certain tris[2-(2-pyridyl)benzimidazole]iron(II) complexes exhibit anomalous magnetic behaviors indicative of the $^5T_2-^1A_1$ crossover.

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.

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%.

* 1771: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.
(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(N₅)₂H₂O: A concentrated aqueous solution of NaN₅ 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)₂H₂O: 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(N₅)₂H₂O coincided with the calculated ones respectively, the Mössbauer spectra of these complexes show that some of Fe(PBI)₂Cl₂ 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 N₅⁻) are listed in Table I. The spectrum of Fe(PBI)₂(CN)₂H₂O 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
T. SHIGEMATSU and Y. SASAKI

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

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

Fig. 1. Infrared spectrum of Fe(PBI)$_2$(CN)$_2$2H$_2$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 2040–2080 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

a trans form. In Fe(PBI)₂(CN)₂2H₂O, 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 Fe(PBI)₂X₂ Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ mm/s</th>
<th>ΔE₀ mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(PBI)₂Cl₂H₂O</td>
<td>1.08</td>
<td>2.63</td>
</tr>
<tr>
<td>Fe(PBI)₂Br₂H₂O</td>
<td>1.06</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe(PBI)₂(N₂)₂H₂O</td>
<td>1.08</td>
<td>2.63</td>
</tr>
<tr>
<td>Fe(PBI)₂(NCS)₂</td>
<td>1.08</td>
<td>2.07</td>
</tr>
<tr>
<td>Fe(PBI)₂(CN)₂2H₂O</td>
<td>0.31</td>
<td>0.74</td>
</tr>
</tbody>
</table>

110 K error = ±0.06 mm/s

Fig. 2. Mössbauer spectra of Fe(PBI)₂X₂ complexes at ca. 110 K.
(a) Fe(PBI)₂Br₂H₂O  (b) Fe(PBI)₂Cl₂H₂O  (c) Fe(PBI)₂(NCS)₂
(d) Fe(PBI)₂(N₂)₂H₂O (e) Fe(PBI)₂(CN)₂2H₂O
The parameters of Fe(PBI)$_2$X$_2$ (X=Cl$^-$, Br$^-$, NCS$^-$, and N$_7^-$) are in the range characteristic of a Fe$^{2+}$ ion in a high-spin form. The spectra of Fe(PBI)$_2$(NCS)$_2$ and Fe(PBI)$_2$(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-dimine 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$_7^-$, 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$_7^-<$NCS$^-<$dipy-$<$phen<CN$^-$. The classification of the other α-dimine 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

The authors wish to thank Dr. T. Shinjo for permitting to use the equipment for the Mössbauer measurement.
REFERENCES

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