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

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Bis[2-(2-pyridyl)imidazole]iron(II) complexes, $Fe(PI)_2X_2$ ($X=Cl^-$, Br^-, NCS^-, N_3^-, and CN^-), were prepared and characterized on the basis of their infrared and Mössbauer spectra and their magnetic data. In $Fe(PI)_2(NCS)_2$, the NCS^- groups are N-bonded and are in a *cis* position. $Fe(PI)_2(CN)_2H_2O$ also has a *cis* configuration about the CN^- ligands. Except for $Fe(PI)_2(CN)_2H_2O$, the magnetic moments of the complexes lie in the 4.94—5.27 B.M. range. $Fe(PI)_2(CN)_2H_2O$ is a diamagnetic compound.

In the series of bis(1,10-phenanthroline)iron(II) complexes, $Fe(phen)_2X_2$, four types of compounds may be classified on the basis of their magnetic properties: (i) if the X ligand gives rise to a weak ligand field, the ground state is $^5T_2$[1]; (ii) if X affords a strong field, the complex is diamagnetic[1]; (iii) if X is F^-, 1/2 mal^{2-}, and 1/2 ox^{2-}, a spin triplet ground state is produced[2,3]; (iv) if $X=NCS^-$ or $NCSe^-$, a transition between the $^5T_2$ and $^1A_1$ ground states is observed at $T_c=174$ and 232 K.[4] In $Fe(bipy)_2(NCS)_2$, such a second-order transition at 216 K has also been reported.[5]

2-(2-Pyridyl)imidazole, possessing the characteristic of α-diimine, gives rise to a slightly weaker ligand field than does 2,2′-bipyridyl in nickel(II) complexes.[6,7] Certain tris[2-(2-pyridyl)imidazole]iron(II) complexes exhibit anomalous magnetic behavior indicative of the $^5T_2$–$^1A_1$ crossover.[8,9]

We have prepared bis[2-(2-pyridyl)imidazole]iron(II) complexes $Fe(PI)_2X_2$ ($X=Cl^-$, Br^-, NCS^-, N_3^-, and CN^-) and investigated their physical properties by means of infrared spectroscopy, Mössbauer-effect, and magnetic-susceptibility measurements; we will report our results here.

Experimental

2-(2-Pyridyl)imidazole was prepared by using a procedure similar to that described by Chiswell, *et al.*[10]

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)imidazole]iron(II), $Fe(PI)_2Cl_2$. The complex was prepared by suspending $Fe(II)(PI)_3Cl_2$-H_2O in 3-methyl-1-butanol and by then refluxing the mixture for 6 hrs. The orange crystals were washed by 3-methyl-1-butanol and were not recrystallized.

(b) Dibromobis[2-(2-pyridyl)imidazole]iron(II), $Fe(PI)_2Br_2$. 2-(2-Pyridyl)imidazole dissolved in acetone was added to a ferrous bromide solution prepared by mixing ferrous sulfate heptahydrate and barium bromide dihydrate solutions. When acetone was added to the filtered solution, orange crystals were precipitated.

(c) Dithiocyanatobis[2-(2-pyridyl)imidazole]iron(II), $Fe(PI)_2(NCS)_2$. A concentrated aqueous solution of NaSCN was added to a mixed solution of $FeCl_24H_2O$ and 2-(2-pyridyl)imidazole. The orange precipitate was washed with an ice-cold acetone-water mixture.

(d) Dicyanobis[2-(2-pyridyl)imidazole]iron(II) Monohydrate, $Fe(PI)_2(CN)_2H_2O$. A concentrated aqueous solution of KCN was added to a filtered solution of $FeCl_24H_2O$ and 2-(2-pyridyl)imidazole. After the acetone has been removed by using an evaporator, reddish-brown crystals were precipitated. One mole of H_2O per mole of the resulting compound was determined by the weight loss at 95 °C over P_2O_5.

(e) Diazidobis[2-(2-pyridyl)imidazole]iron(II), $Fe(PI)_2(N_3)_2$. A concentrated aqueous solution of NaN_3 was added to the filtered starting solution, and the wine-red crystals thus precipitated were washed by water.

The analytical results of these complexes are given in Table 1. The quantitative determination of N in $Fe(PI)_2(N_3)_2$ met with difficulties.

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

Magnetic Measurements. The magnetic susceptibilities were measured with a torsion-balance magnetometer. All the measurements were made at two different field strengths; no field dependence of the magnetic susceptibility was observed. The molar susceptibilities were corrected for diamagnetism, the following corrections: Fe^{2+}, -13; H_2O, -13; Cl^-, -23.4; Br^-, -34.6; NCS^-, -31.0; CN^-, -13; N_3^-, -13.7; 2-(2-pyridyl)imidazole, -82 (in units of 10^{-6} cgs/mol). The effective magnetic moment, μ_{eff}, was obtained from the $\mu_{eff}=2.828\sqrt{\chi_M'T}$ relation, χ_M' being the fully corrected molar susceptibility, and T, the temperature in K.

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

Table 1. Analytical results (amounts in %)

Complex	C		H		N		Fe	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$Fe(PI)_2Cl_2$	45.78	46.07	3.42	3.38	19.59	20.15	12.66	13.39
$Fe(PI)_2Br_2$	37.97	37.98	2.80	2.97	16.45	16.61	10.81	11.04
$Fe(PI)_2(NCS)_2$	46.74	46.76	2.83	3.05	23.69	24.24	11.46	12.08
$Fe(PI)_2(CN)_2H_2O$	51.46	51.94	3.66	3.88	26.33	26.93	13.11	13.42
$Fe(PI)_2(N_3)_2$	44.45	44.66	3.17	3.28	37.46	39.08	12.29	12.98

measurements. The velocity scale was calibrated with metallic iron, and the velocity was determined to an accuracy of ±0.04 mm/s.

Results and Discussion

Infrared Spectra. The frequencies of the band maxima of the X ligands in the $Fe(PI)_2X_2$ complexes ($X=NCS^-$, CN^-, and N_3^-) are listed in Table 2. Since the absorption bands due to the 2-(2-pyridyl)-imidazole of these complexes change little from those of $Fe(PI)_2Cl_2$ and $Fe(PI)_2Br_2$, it is easy to assign the bands due to the X ligands.

Table 2. Infra-red frequencies of ligands X in $Fe(PI)_2X_2$ complexes (in cm^{-1})

Complex	Frequencies of band maxima	Assignment
$Fe(PI)_2(NCS)_2$	2071 vs, 2083 vs	C–N stretching
	975 s	C–S stretching
	460 m	N–C–S bending
$Fe(PI)_2(CN)_2H_2O$	2043 vs, 2051 vs	C–N stretching
$Fe(PI)_2(N_3)_2$	2037 vs, 2056 vs	N–N stretching

The thiocyanate group has three fundamental frequencies, *i.e.*, ν_1 (C–N stretching), ν_2 (N–C–S bending), and ν_3 (C–S stretching). Since thiocyanate is a bifunctional ligand, the positions of ν_1, ν_2, and ν_3 depend on whether this group is attached to the metal ion through N or through S. In $Fe(PI)_2(NCS)_2$, ν_1, ν_2, and ν_3 are in the range characteristic of N-bonded thiocyanate.[11–13] A splitting of the C–N stretching mode is observed. A *cis* configuration has been reported for both $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$, which exhibit splittings of the C–N stretching band of 12 and 10 cm^{-1} respectively[4,5] as well as for $Fe(phen)_2(CN)_2$, where the C–N stretching shows two peaks at 2075 and 2062 cm^{-1}.[14] In $Fe(PI)_2(NCS)_2$, the splitting of the C–N stretching mode is, therefore, taken as an indication of a *cis* configuration about the thiocyanate ligands. In $Fe(PI)_2(CN)_2H_2O$, the splitting of the C–N stretching mode is also observed. Therefore, this complex may have a *cis* configuration about the cyano ligands. Though $Fe(PI)_2(CN)_2H_2O$ is a low-spin compound, as will be described later, the absorption bands due to 2-(2-pyridyl)imidazole are similar to those of other complexes.

Magnetic Data. The results of magnetic-susceptibility measurements of polycrystalline samples between 77.2 and 283.0 K are compiled in Table 3. Except for $Fe(PI)_2(CN)_2H_2O$, the magnetic moments of the present complexes are characteristic of an iron(II) ion in a $^5T_2$ ground state. Within the temperature range of 77.2—283.0 K, the susceptibilities follow the Curie-Weiss law, $\chi_M'=C/(T-\Theta)$. The resulting values of the Weiss constant are included in Table 3. The magnetic moment observed in $Fe(PI)_2(CN)_2H_2O$ is indicative of a $^1A_1$ ground state of iron(II).

Mössbauer Spectra. The Mössbauer parameters are listed in Table 4. Some typical spectra of $Fe(PI)_2(N_3)_2$ are shown in Fig. 1. It was impossible to

Table 3. Magnetic data of $Fe(PI)_2X_2$ complexes

Compound	Temp. (K)	$10^6\chi_M'$ (cgs/mol)	μ_{eff} (B.M.)	Θ (K)
$Fe(PI)_2Cl_2$	77.2	39600	4.94	−7
	103.8	29879	4.98	
	141.3	22250	5.01	
	190.2	16836	5.06	
	236.5	13636	5.08	
	283.0	11545	5.11	
$Fe(PI)_2Br_2$	77.2	41502	5.06	−9
	103.8	31217	5.09	
	141.3	23503	5.15	
	190.2	17894	5.22	
	236.5	14504	5.24	
	283.0	12284	5.27	
$Fe(PI)_2(NCS)_2$	77.2	39725	4.95	−7
	103.8	30169	5.00	
	141.3	22326	5.02	
	190.2	16917	5.07	
	236.5	13762	5.10	
	283.0	11598	5.12	
$Fe(PI)_2(N_3)_2$	77.2	41535	5.06	−6
	103.8	31455	5.11	
	141.3	23502	5.15	
	190.2	17901	5.22	
	236.5	14317	5.20	
	283.0	12077	5.23	
$Fe(PI)_2(CN)_2H_2O$	77.2	279	0.42	—
	103.8	256	0.46	
	141.3	238	0.52	
	190.2	224	0.58	
	236.5	218	0.64	
	283.0	212	0.69	

Table 4. Mössbauer parameters δ^{IS} and ΔE_Q (in mm/s)

Compound	Temp. (K)	δ^{IS} (mm/s)	ΔE_Q (mm/s)
$Fe(PI)_2Cl_2$	298	1.03	2.64
	77.2	1.14	3.04
$Fe(PI)_2Br_2$	298	—	—
	110	1.27	3.05
$Fe(PI)_2(NCS)_2$	298	1.01	2.65
	77.2	1.09	2.94
$Fe(PI)_2(N_3)_2$	298	1.01	1.25
	77.2	1.15	2.24
$Fe(PI)_2(CN)_2H_2O$	298	0.21	0.11
	77.2	0.32	0.18

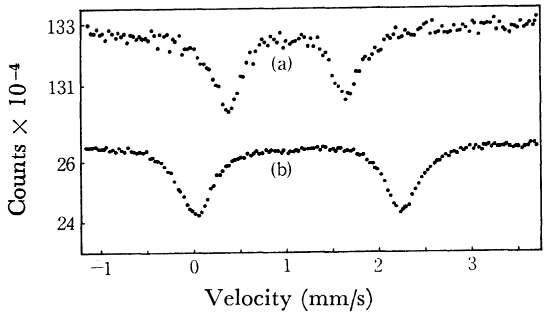

Fig. 1. Mössbauer spectra of $Fe(PI)_2(N_3)_2$.
a: 298 K b: 77.2 K

observe the Mössbauer effect of $Fe(PI)_2Br_2$ at 298 K. The parameters of $Fe(PI)_2X_2$ ($X=Cl^-$, Br^-, NCS^-, and N_3^-) are in the range characteristic of a Fe^{2+} ion in a high-spin form.[15] The spectra of $Fe(PI)_2(N_3)_2$ show marked features in the magnitude and the temperature dependency of the quadrupole splitting. In addition, the spectrum at 298 K exhibits a difference in the peak intensity of the doublet lines. The variation with the temperature predicts that there is an anisotropic recoilless fraction in this complex. On the other hand, the parameters of $Fe(PI)_2(CN)_2H_2O$ are characteristic of an iron(II) ion in a low-spin form.

The bis[2-(2-pyridyl)imidazole]iron(II) complexes, $Fe(PI)_2X_2$, may be classified into three groups on the basis of their magnetic properties: (i) if $X=Cl^-$, Br^-, NCS^-, and N_3^-, $Fe(PI)_2X_2$ is a high-spin compound; (ii) $Fe(PI)_2(CN)_2H_2O$ is a diamagnetic complex; (iii) $[Fe(PI)_3]^{2+}$ complexes in which $X=1/2$[2-(2-pyridyl)-imidazole] exhibit a spin equilibrium between $^1A_1$ and $^5T_2$ states.[8,9] The tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridyl)iron(II) complexes are diamagnetic compounds, and $Fe(phen)_2(NCS)_2$ and $Fe(bipy)_2(NCS)_2$ have an anomalous magnetic property due to a $^1A_1$ and $^5T_2$ crossover.[4,5] Such a change in the spin state from ligand to ligand indicates that 2-(2-pyridyl)-imidazole gives rise to a weaker ligand field than do 1,10-phenanthroline and 2,2′-bipyridyl in iron(II) complexes.

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