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Synthesis and Characterization of Iron(III) Complexes with Unsymmetrical Quadridentate Schiff Bases, and Spin Equilibrium Behavior in Solution[1)]

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Several iron(III) complexes with planar unsymmetrical quadridentate Schiff bases composed of 1:1:1 condensation products of acetylacetone, ethylenediamine, and each of salicylaldehyde and *o*-hydroxyacetophenone have been prepared and characterized, where the Schiff bases are abbreviated as [H_2salacen] and [H_2hapacen], respectively. The effective magnetic moment of [FeCl(hapacen)] increases gradually from 3.46 BM at 80 K to 5.31 BM at 301 K, and was interpreted by a spin-spin interaction model based on a binuclear structure with an antiferromagnetic interaction parameter of $J=-10\ \mathrm{cm}^{-1}$ ($S_1=S_2=5/2$), while the magnetic moment for [FeCl(salacen)] is 5.86 BM at 80 K and 5.96 BM at 302 K, indicating that the complex is a monomeric species of high-spin type. The bis(imidazole)iron(III) complexes [Fe(im)$_2$(salacen)]BPh$_4\cdot$CH$_3$OH and [Fe(im)$_2$(hapacen)]BPh$_4\cdot$2CH$_3$OH showed a striking thermochromic behavior in various organic solvents, changing from dark red to green with decrease of the temperature. The complexes are essentially of low-spin type in solids, where im and BPh$_4$ denote imidazole and tetraphenylborate, respectively. Electronic, ^{1}H NMR (Evans method), and ESR spectra confirmed that the thermochromism is caused by spin-equilibrium between high-spin($S=5/2$) and low-spin($S=1/2$) states of iron(III).

Several iron(III) complexes such as tris(dialkyldithiocarbamato)iron(III) and iron(III) complexes with hexadentate Schiff bases or porphyrin derivatives have been known as examples of cross-over complexes in solids.[2)] Spin-equilibrium behavior attributable to high-spin($S=5/2$)$\rightleftharpoons$low-spin($S=1/2$) of iron(III) in solution has been observed in iron(III) hemoproteins such as methemoglobin and cytochrome peroxidase,[3)] and synthetic iron(III) complexes with hexadentate Schiff bases.[4)] In order to develop a model complex for the spin-equilibrium behavior of natural products, it is desirable to study iron(III) complexes with planar quadridentate ligands exhibiting spin-equilibrium in solution.

Nishida *et al.*[5)] investigated the magnetic properties of the iron(III) complexes [Fe(im)$_2$(sal$_2$en)]BPh$_4$ and [Fe(im)$_2$(ac$_2$en)]BPh$_4$ with ligand structures of **1** and **3** of Fig. 1, and elucidated that the complexes [Fe(im)$_2$(sal$_2$en)]BPh$_4$ and [Fe(im)$_2$(ac$_2$en)]BPh$_4$ are of high-spin and low-spin type in solids, respectively. When the discussion is limited to bis(imidazole)iron(III) complexes with similar types of ligand systems, a complex with a ligand field strength intermediate between those of **1** and **3** is expected to be a candidate for a spin cross-over complex. The in-plane ligand field strength can be estimated by the positions of d-d band maxima of the corresponding copper(II) complexes, where the d-d band maxima of the copper(II) complexes are given in parentheses in Fig. 1.[6)] The position of the d-d band maximum of the unsymmetrical quadridentate copper(II) complex of **2** is intermediate between those of **1** and **3**, as would be predicted by the ligand structures. Based on the criterion described above, the ligands **4** and **5**,

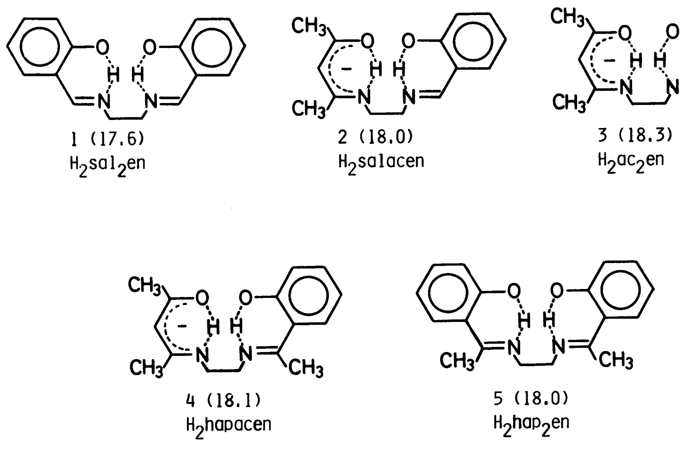

Fig. 1. Structures of [H$_2$sal$_2$en] (**1**), [H$_2$salacen] (**2**), [H$_2$ac$_2$en] (**3**), [H$_2$hapacen] (**4**), and [H$_2$hap$_2$en] (**5**). The positions of d-d band maxima of the corresponding copper(II) complexes are given in parentheses (10^3 cm^{-1}).

in addition to the ligand **2**, were selected, where the structures of the ligands, along with the positions of d-d band maxima of the corresponding copper(II) complexes in parentheses, are shown in Fig. 1.

In this study, bis(imidazole)iron(III) complexes with ligands **2**, **4**, **5** along with their chloro iron(III) complexes, were prepared and characterized by elemental analyses, melting points, magnetic susceptibilities, and ESR spectra. The bis(imidazole)iron(III) complexes with unsymmetrical quadridentate ligands (**2**, **4**) showing a striking thermochromism in solution were investigated by electronic, ESR, and ^{1}H NMR (Evans method)[7] spectra.

Experimental

Physical Measurements. Melting points were measured on a Yanagimoto melting points apparatus and are uncorrected. Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGC-20 type microthermobalance at a heating rate of 5 °C min^{-1}, using *ca.* 10 mg of a sample for each run. Magnetic moments for the bis(imidazole)iron(III) complexes in dichloromethane were obtained by using the Evans ^{1}H NMR technique at ambient temperature (28 °C),[7] a JEOL MH 100 spectrometer being used at 100 MHz. Electronic spectra in Nujol mull were recorded on a Shimadzu spectrophotometer UV 200, while electronic spectra in solution at room temperature and *ca.* 200 K were recorded on a Hitachi recording spectrophotometer 323, where a jacketed, insulated quartz cell was used, and the temperature was monitored by a YEW Type 2572 digital thermometer. Variable temperature spectra were obtained on a Hitachi 340 spectrophotometer, where the temperature of a sample solution was thermostated within ±0.1 °C by use of a temperature controlled circulating bath, Neslab RTE-8, and measured immediately before and after each spectral measurement with a copper-constantan thermocouple and a digital thermometer, Takeda TR-2121.[8] ESR spectra were measured at ambient temperature and liquid nitrogen temperature on a JEOL JES-FEAX (X-band), using Mn^{2+} doped in MgO as reference. Magnetic susceptibilities on polycrystalline samples were determined by the Faraday method, using an electrobalance Type 2002 (Cahn Instrument) with an electromagnet (8000 G) operated at 20 A. The temperature was controlled over 78—300 K by using a digital temperature controller, Model 3700 (Scientific Instrument). $HgCo(NCS)_4$ was used as a calibration substance. The effective magnetic moment was calculated by the formula of $\mu_{\mathrm{eff}}=2.828\sqrt{\chi_{\mathrm{A}}T}$, where χ_{A} is a molar susceptibility after diamanetic correction.

Synthesis. *Ligands.* Unsymmetrical quadridentate Schiff base ligands (**2**, **4**) were prepared by the demetallation reaction of the corresponding copper(II) complexes with gaseous hydrogen sulfide in dichloromethane solution, according to the method reported earlier,[9] and identified by the ^{1}H NMR spectra. Symmetrical quadridentate Schiff base **5** was prepared by the method of literature.[10]

Chloroiron(III) Complexes. The preparative methods of the chloroiron(III) complexes [FeCl(salacen)], [FeCl(hapacen)], and [FeCl(hap$_2$en)] are similar, so that only the synthesis of [FeCl(salacen)] is described in detail. To a solution of [H$_2$salacen] (10 mmol) in 50 cm^3 of absolute methanol was added a solution of anhydrous iron(III) chloride (10 mmol) in 50 cm^3 of absolute methanol. To this mixture, triethylamine (20 mmol) was added. The resulting solution was stirred at 60 °C for 1 h and allowed to stand for several hours at room temperature. The black crystals which separated were filtered, washed with absolute methanol and diethyl ether, and dried *in vacuo*.

Bis(imidazole)iron(III) Complexes. The preparative methods of the bis(imidazole)iron(III) complexes [Fe(im)$_2$(salacen)]BPh$_4$, [Fe(im)$_2$(hapacen)]BPh$_4$, and [Fe(im)$_2$(hap$_2$en)]BPh$_4$ are similar, and only the synthesis of [Fe(im)$_2$(salacen)]BPh$_4$ is exemplified in detail. The mixture of [FeCl(salacen)] (2 mmol) and imidazole (4 mmol) in 150 cm^3 of absolute methanol was stirred at 60 °C for 20 min, and the solution was filtered while hot. The filtrate was added to a solution of sodium tetraphenylborate (30 mmol) in 10 cm^3 of absolute methanol, and the resulting red solution was allowed to stand overnight to precipitate green crystals. The green needle crystals were filtered, washed with a small amount of absolute methanol and diethyl ether, and dried *in vacuo*. They were recrystallized from a mixture of dichloromethane and absolute methanol.

Results and Discussion

Analytical data and melting points are given in Table 1. As indicated by the elemental analyses, the bis(imidazole) iron(III) complexes tend to crystallize as solvates. The number of solvent molecule of crystallization was evaluated by thermogravimetric analysis (TGA), where the weight losses estimated by the elemental analyses were observed.

Magnetic Properties in Solids. *Chloroiron(III) Complexes.* The value of the effective magnetic moment of [FeCl(salacen)] is 5.86 BM at 80 K and 5.96 BM at 302 K, indicating that the complex is a mononuclear species with a high-spin state of iron(III). On the other hand, the effective magnetic moment of [FeCl(hapacen)] increases gradually from 3.46 BM at 80 K to 5.31 BM at 302 K (see Fig. 2). Magnetic susceptibility data for [FeCl(hapacen)] were analyzed with

TABLE 1. ELEMENTAL ANALYTICAL DATA AND MELTING POINTS[a)]

Compound	C (%)	H (%)	N (%)	Mp θ_{m}/°C
[FeCl(salacen)]	49.69 (50.11)	4.82 (4.81)	8.19 (8.35)	213
[FeCl(hapacen)]	51.49 (51.53)	5.27 (5.09)	7.82 (8.01)	244
[FeCl(hap$_2$en)]	54.41 (54.64)	4.86 (5.31)	6.97 (6.91)	>290
[Fe(im)$_2$(salacen)]BPh$_4$·CH$_3$OH	68.77 (68.63)	6.00 (6.14)	10.69 (10.67)	125
[Fe(im)$_2$(hapacen)]BPh$_4$·2CH$_3$OH	67.33 (67.72)	6.26 (6.53)	9.94 (10.08)	118
[Fe(im)$_2$(hap$_2$en)]BPh$_4$·2CH$_3$OH	68.81 (69.06)	6.09 (6.26)	9.82 (9.66)	131

a) Calcd values are in parentheses.

a spin-spin interaction model based on the spin Hamiltonian $-2JS_1 \cdot S_2$ ($S_1=S_2=5/2$). The susceptibility per iron atom of a binuclear species is given in Eq. 1.[11)]

$$\chi_A = Ng^2\beta^2[55+30\exp(10x)+14\exp(18x)+5\exp(24x) +\exp(28x)]/kT[11+9\exp(10x)+7\exp(18x) +5\exp(24x)+3\exp(28x)+\exp(30x)] \quad (x=-J/kT) \qquad (1)$$

Assuming an isotropic g value of 2.00, the J value obtained by the best-fit of the susceptibility data to Eq. 1 is $-10\ \mathrm{cm}^{-1}$.[12)] Figure 2 shows the experimental effective magnetic moments and the theoretical curve with the bast-fit value of J. The J value of $-10\ \mathrm{cm}^{-1}$ is comparable to the J values of chloro(*N*,*N*-disalicylidene-ethylenediaminato)iron(III) ([FeCl(sal$_2$en)]) and analogous complexes.[13)] Figure 3 shows a proposed structure of [FeCl(hapacen)], based on the structure of [FeCl(sal$_2$en)].[13)]

Bis(imidazole)iron(III) Complexes. The effective magnetic moments for [Fe(im)$_2$(salacen)]BPh$_4$·CH$_3$OH and [Fe(im)$_2$(hapacen)]BPh$_4$·2CH$_3$OH are 3.02 and 3.20 BM at 301 K, respectively, indicating that the complexes are essentially of low-spin type in the solid state. ESR spectra for [Fe(im)$_2$(salacen)]-BPh$_4$·CH$_3$OH and [Fe(im)$_2$hapacen]BPh$_4$·2CH$_3$OH in the solid state showed a single signal at *ca.* g=2.1 at 298 K, and the signal split into three components at liquid nitrogen temperature, which is characteristic of low-spin iron(III) complexes.[14)] Experimental anisotropic g values are listed in Table 2. The nature of the ground state Kramers doublet of the ^{2}T of pseudo-octahedral iron(III) complexes can be elucidated by using the anisotropic g values. In this calculation, the spin-orbit coupling interaction and the crystal field distortion are considered. The eigenfunctions of a $(t_2)^1$ configuration may be written as

$$\Psi_i^+ = A_i|1^+> +B_i|\zeta_1^-> +C_i|-1^+>$$
$$\Psi_i^- = A_i|-1^-> -B_i|\zeta_1^+> +C_i|+1^->,$$

where $|1>=-(d_{xz}+id_{yz})/\sqrt{2}$, $|-1>=(d_{xz}-id_{yz}).\sqrt{2}$, $|\zeta_1>=id_{xy}$, i=1, 2, 3, and the superscripts + and − mean the α-spin and β-spin wave functions. The Kramers doublet will be split by the magnetic field interaction $\mathbf{H}=\beta(k\hat{\mathbf{l}}+2\hat{\mathbf{s}})\mathbf{H}$, where k, the orbital reduction factor, is fixed at 0.9 in this calculation. The g values for the ground state level may be given as[14)]

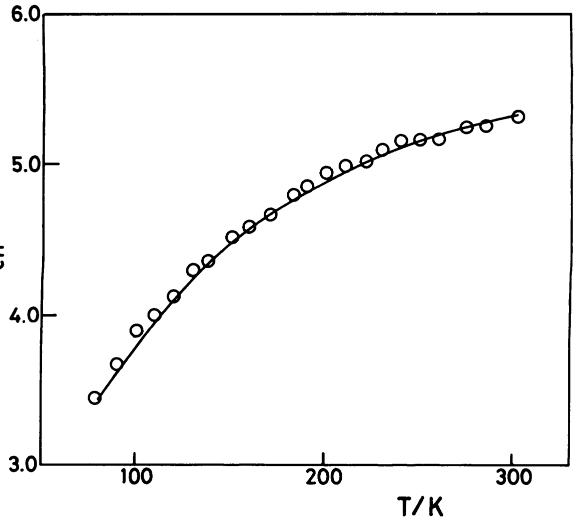

Fig. 2. Temperature dependence of the effective magnetic moment for [FeCl(hapacen)] (o), where the solid line represents theoretical curve of Eq 1 with the parameters of J= 10 cm^{-1} and g=2.00.

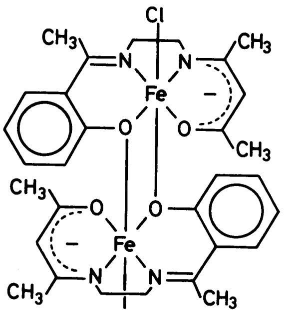

Fig. 3. A proposed structure for [FeCl(hapacen)].

Table 2. ESR parameters and occupied orbital of unpaired electron for [Fe(im)$_2$(salacen)]BPh$_4$·CH$_3$OH (**1**) and [Fe(im)$_2$(hapacen)]BPh$_4$·2CH$_3$OH (**2**)

	(**1**)	(**2**)
g_x	2.349	2.322
g_y	2.138	2.155
g_z	1.938	1.931
A_1	0.104	0.105
B_1	0.995	0.993
C_1	−0.036	−0.028
unpaired electron orbital	d_{xy}	d_{xy}

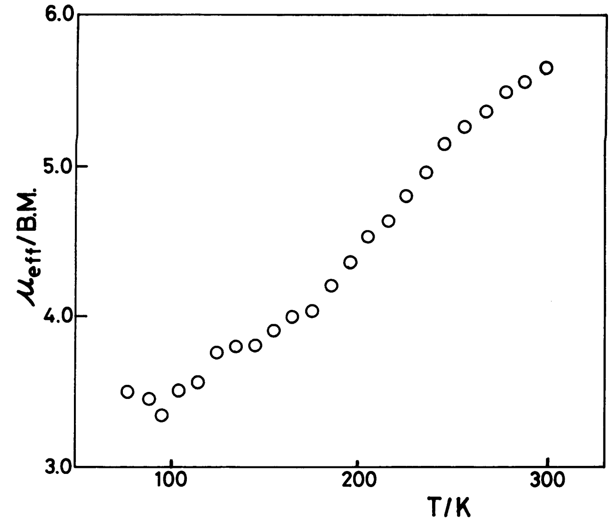

Fig. 4. Temperature dependence of the effective magnetic moment for [Fe(im)$_2$(hap$_2$en)] BPh$_4$·2CH$_3$OH (O).

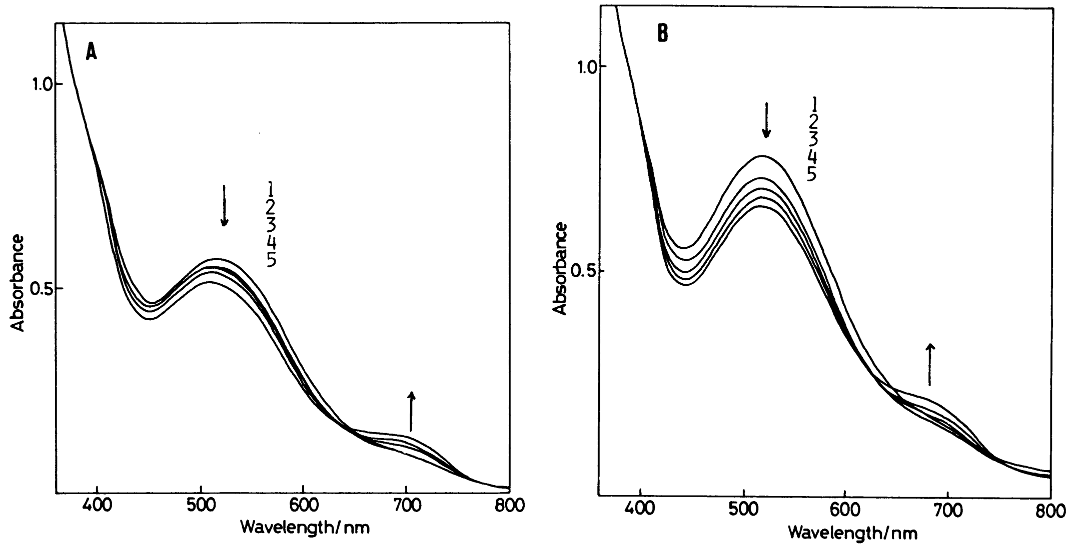

Fig. 5. Absorption spectra of $[Fe(im)_2(salacen)]\ BPh_4 \cdot CH_3OH$ (**A**) (3.098×10^{-4} mol dm^{-3}) and $[Fe(im)_2(hapacen)]BPh_4 \cdot 2CH_3OH$ (**B**) (2.735×10^{-4} mol dm^{-3}) in dichloromethane solution at various temperatures (301 (**1**), 288 (**2**), 273 (**3**), 263 (**4**), 251 (**5**) K).

$$g_z = 2[A^2 - B^2 + C^2 + k(A^2 - C^2)]$$
$$g_x = 2[B^2 - 2AC + \sqrt{2}kB(A - C)]$$
$$g_y = 2[B^2 + 2AC + \sqrt{2}kB(A + C)]$$
$$A^2 + B^2 + C^2 = 1$$

The values of A, B, and C are selected to solve the above equations by using the experimental anisotropic g values. Since the signs of the observed g values are not determined experimentally, the values of A, B, and C are not obtained unequivocally, so that it is necessary to try many assignments to solve the equations. The reasonable solutions[14] are selected and listed in Table 2. As shown in Table 2, the ground state Kramers doublet consists mainly of the state wherein the unpaired electron remains in the d_{xy} orbital, because the B value is nearly equal to 1.

Figure 4 shows the temperature dependence of the magnetic moment of $[Fe(im)_2(hap_2en)]BPh_4 \cdot 2CH_3OH$ in the solid state. The value of the effective magnetic moment increases gradually from 3.50 BM at 78 K to 5.64 BM at 298 K. This behavior is attributable to a spin-equilibrium between high-spin an low-spin states of iron(III).

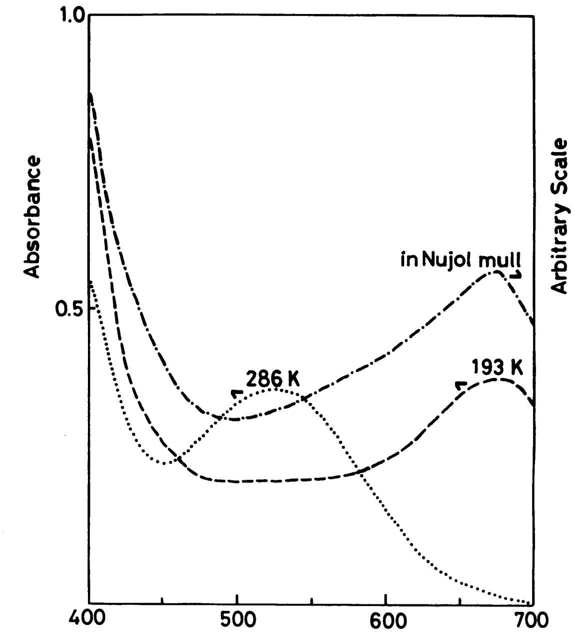

Fig. 6. Electronic absorption spectra of $[Fe(im)_2(hapacen)] \cdot 2CH_3OH$ in dichloromethane at 286 and 193 K, along with the spectrum in Nujol mull.

Thermochromic Behavior in Solution. Green needle crystals of $[Fe(im)_2(salacen)]BPh_4 \cdot CH_3OH$ and $[Fe(im)_2(hapacen)]BPh_4 \cdot 2CH_3OH$ are dissolved in various organic solvents such as acetone, dichloromethane, chloroform, N,N-dimethylformamide, and acetonitrile, to change their colors to dark red at room temperature. At *ca.* 200 K (Dry Ice/acetone bath), the color changes from dark red to green, showing a striking thermochromic behavior. It should be noted that such a thermochroism was not observed for the symmetrical complexes $[Fe(im)_2(sal_2en)]BPh_4$ and $[Fe(im)_2(hap_2en)]BPh_4 \cdot 2CH_3OH$. Temperature dependence of the electronic spectra of $[Fe(im)_2(salacen)]BPh_4 \cdot CH_3OH$ and $[Fe(im)_2(hapacen)]BPh_4 \cdot 2CH_3OH$ in dichloromethane over the temperature range of *ca.* 300—250 K is shown in Fig. 5. The spectrum of $[Fe(im)_2(hapacen)]BPh_4 \cdot 2CH_3OH$ in dichloromethane at 286 and 193 K, along with the spectrum in Nujol mull at room temperature is shown in Fig. 6. As shown in Fig. 5 and 6, the spectrum of $[Fe(im)_2(hapacen)]BPh_4 \cdot 2CH_3OH$ at 300 K exhibits an absorption band at 520 nm with an extinction coefficient on the order of *ca.* 2500 mol^{-1} dm^3 cm^{-1}. With a lowering of the temperature, this band decreases its intensity and a new band appears at 680 nm. The electronic spectrum of [Fe(im)$_2$(hapacen)]BPh$_4$·2CH$_3$OH at 193 K in dichloromethane resembles that in Nujol mull at room temperature, where the complex is confirmed to be a low-spin type in the solid state on the basis of the magnetic moment and the ESR spectrum, as described earlier. Therefore the lower energy band around 680 nm is due to a low-spin species. The magnetic moments for [Fe(im)$_2$(salacen)]BPh$_4$·CH$_3$OH and [Fe(im)$_2$(hapacen)]BPh$_4$·2CH$_3$OH in dichloromethane at 301 K were estimated by the Evans ^{1}H NMR method to be 5.45 and 5.60 BM, respectively, which lie in the range expected for high-spin iron(III) complexes, so that the higher energy band around 520 nm is due to a high-spin species.

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