CHEMISTRY LETTERS, pp. 479 - 480, 1984.

SPIN STATE EQUILIBRIUM OF IRON(III) COMPLEX WITH PLANAR UNSYMMETRICAL QUADRIDENTATE SCHIFF BASE IN SOLUTION

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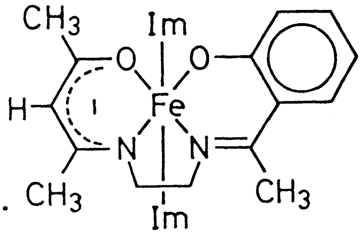
New iron(III) complex containing planar unsymmetrical quadridentate Schiff base, $[\mathrm{FeIm_2L}]\mathrm{B\phi_4}$, showed a striking thermochromism in solution, changing from dark red to green with decrease of the temperature, where Im, L, and $\mathrm{B\phi_4}$ denote imidazole, N-hydroxyacetophenone-N'-acetylacetone-ethylenediimine, tetraphenylborate, respectively. The electronic and ESR spectra established that the thermochromism is caused by the spin equilibrium between high spin(S=5/2) and low spin(S=1/2) of iron(III).

Spin equilibrium behavior attributable to high spin(S=5/2) $\rightleftarrows$ low spin(S=1/2) of iron(III) in solution has been observed in ferric hemoproteins$^{1)}$ such as methemoglobin, and cytochrome peroxidase, and synthetic iron(III) complexes with hexadentate Schiff base.$^{2)}$ In order to develop the model complex for the spin equilibrium behavior in natural products, it should be desired to study synthetic iron(III) complex with planar quadridentate ligand exhibiting spin equilibrium in solution. We report here a spin equilibrium system of the iron(III) complex composed of planar unsymmetrical quadridentate Schiff base and imidazoles ($[\mathrm{FeIm_2L}]^+$, see figure), as an initial attempt to develop the model system.


$[\mathrm{FeIm_2L}]^+$

The unsymmetrical quadridentate Schiff base was prepared by the demetallation reaction of the corresponding copper(II) complex with hydrogen sulfide according to the procedure of Kuska et al.$^{3)}$ and Howells et al.$^{4)}$ Found: C,69.12; H, 7.77; N, 10.66%. Calcd for $\mathrm{C_{15}H_{20}N_2O_2}$: C, 69.20; H, 7.74; N, 10.76%. Mp 139 °C. [FeClL]: The $[\mathrm{H_2L}]$ ligand (20 mmol) dissolved in 50 cm^3 of absolute methanol was added to anhydrous iron(III) chloride (20 mmol) dissolved in 50 cm^3 of absolute methanol. To this mixture, triethylamine (40 mmol) was added. The resulting solution was warmed at 60 °C for 15 min and subsequently allowed to stand for several hours at room temperature. The black crystals yielded were filtered, washed with absolute methanol and ether, and dried in vacuo. Found: C, 51.49; H, 5.27; N, 7.87%. Calcd for $\mathrm{C_{15}H_{18}N_2O_2ClFe}$: C, 51.53; H, 5.19; N, 8.01%. Mp 245 °C.

[FeIm$_2$L]Bϕ_4: The mixture of [FeClL] (10 mmol) and imidazole (30 mmol) was suspended in absolute methanol and warmed at 60 °C for 1 h. The resulting solution was poured into 10 cm^3 of absolute methanol solution of sodium tetraphenylborate (15 mmol) to precipitate green crystals from red solution. They were collected and recrystallized from a mixture of absolute methanol and chloroform. Found: C, 67.83; H, 6.26; N, 9.94%. Calcd for $C_{45}H_{46}N_6BO_2Fe\cdot 2CH_3OH$: C, 67.33; H, 6.25; N, 10.10%. Mp 155 °C.

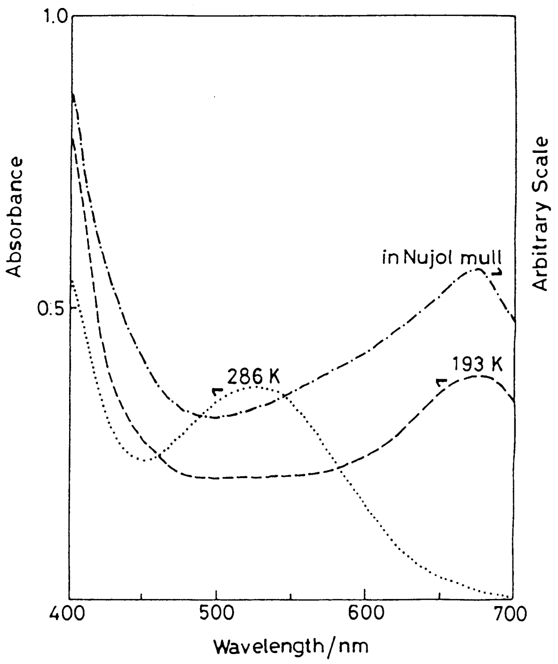


Fig. 1. Electronic spectra of [FeIm$_2$L]Bϕ_4.

The complex [FeIm$_2$L]Bϕ_4 was reversibly thermochromic in solution, changing from dark red at room temperature to green at ca. 200 K in various organic solvents. The electronic spectra in dichloromethane at 286 and 193 K, along with the spectrum in Nujol mull are shown in Fig. 1. At room temperature, the spectrum exhibited a band at 520 nm with an extinction coefficient on the order of 2500 mol^{-1}dm^{3}cm^{-1}. With decreasing temperature, this band decreased its intensity and a new band appeared at 685 nm. The temperature dependency of the spectrum explains striking thermochromic behavior in solution. The ESR spectrum in dichloromethane at room temperature showed broad absorptions over the wide range of 1500-3500 G, being characteristic of high spin iron(III) complexes.$^{5)}$ The data suggest that the band around 520 nm is an indicative of high spin species. The magnetic moment in solid state was measured by Faraday method to be 3.20 BM at 301 K, indicating that the complex is essentially low spin in solid state. The ESR spectrum in solution at 78 K showed three sharp peaks around 3000 G (g_1=2.322, g_2=2.155, g_3=1.931), indicating that an unpaired electron is occupied in d_{xy} orbital.$^{6)}$ The electronic spectrum in Nujol mull at room temperature resembles to the solution spectrum at 193 K. The data suggest that the lower energy band around 685 nm is due to low spin species.

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(Received December 5, 1983)