

Electron Paramagnetic Resonance of Protohemin Dimethyl Ester Complexes with Sterically Hindered Imidazole Derivatives

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In a previous work [1], it was spectrophotometrically shown that the addition reaction of hindered imidazole (B) such as 2-methyl-, 2,4-dimethyl-, 2-ethyl-, 1,2-dimethylimidazole with (protoporphyrin IX dimethyl ester) iron(III) chloride (Fe(PPDME)Cl) proceeds in two steps to give the bis-adduct, Fe(PPDME)₂Cl, which exhibits the low-spin type spectrum similar to that of the bis-adduct with unhindered imidazole. It was reported by Satterlee *et al.* [2] that the addition of 2-methyl- and 1,2-dimethylimidazole to the mesotetraphenylporphyrin iron(III) chloride solution yields proton NMR spectra attributable to the low-spin bis-adduct formation. These results indicate that two molecules of the hindered imidazole can coordinate axially to porphyrin iron(III) to yield a low-spin complex, irrespective of the steric interaction between the porphyrin core and the substituent adjacent to the bonding nitrogen. By the measurements of EPR spectra at 77 K, however, the low-spin state of the iron(III) has not been defined in porphyrin iron(III) solution containing 2-methyl- or 1,2-dimethylimidazole [2, 3]. The porphyrin iron(III) complexes with hindered imidazoles have been isolated as mono-adducts, whereas those with unhindered imidazoles have been isolated as bis-adducts [4]. In this note, we wish to report on the results of EPR measurements at 77 K in both frozen glass and solid states for Fe(PPDME)Cl-hindered imidazole system (hindered imidazoles: 2-methyl-, 2-ethyl-, 2-phenyl-, 2,4-dimethyl-, and 1,2-dimethylimidazole); these results are compared with those for Fe(PPDME)Cl-unhindered imidazole system.

The EPR spectra of the complex with hindered imidazole in chloroform vary with the concentration of the base. As shown in Fig. 1, the high-spin type signal at around $g = 6$ is much stronger in the lower molar ratio of [B]/[Fe(PPDME)Cl], whereas the low-spin type signal with three distinct g -values at around $g = 2$ appears in the higher molar ratio. The base concentration dependence of the spectra for 2,4-dimethyl- and 2-ethylimidazole is virtually identical with that for 1,2-dimethylimidazole in Fig. 1, though the low-spin signal for 2-ethylimidazole is markedly weak in intensity. In the case of 2-methylimidazole,

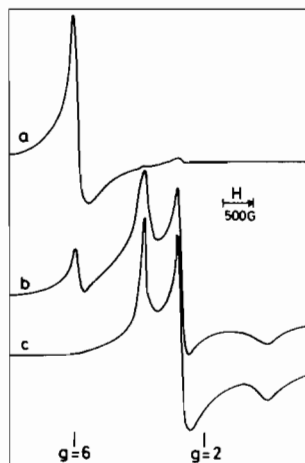


Fig. 1. The EPR spectra for the Fe(PPDME)Cl-1,2DMeIm system in chloroform at 77 K: [1,2DMeIm]/[Fe(PPDME)Cl] = (a) 2, (b) 10, (c) 200.

only a very weak high-spin signal is observed in molar ratios from 2 to 100. This situation for 2-methylimidazole remains unaltered in various solvents such as chloroform, chloroform-ethanol (1:9, v/v), dimethylformamide, and dimethylformamide-chloroform (4:1, v/v). In the case of 2-phenylimidazole, only an intense high-spin signal similar to that in Fig. 1(a) is observed through the molar ratio of 30, which is consistent with the result that the bis-adduct formation is not found in the study of the visible absorption spectra for this system [1].

The EPR spectrum at 77 K for the solid, which is prepared by fusion of hindered imidazole with Fe(PPDME)Cl and then by cooling to room temperature, is similar to that for the frozen glass in the higher molar ratios for 2-ethyl-, 2-phenyl-, 2,4-dimethyl-, and 1,2-dimethylimidazole, whereas such a similarity is not found for 2-methylimidazole. For the Fe(PPDME)Cl-2-methylimidazole system, a broad and weak signal with a maximum slope at around $g = 2.3$ is observed together with a weak high-spin one, though its origin is ambiguous.

The bis-adduct formation constant of (protoporphyrin IX dimethyl ester) iron(III) complexes with hindered imidazoles in chloroform decreases in the order of bases: 2-methyl- \approx 2,4-dimethyl- > 2-ethyl- > 1,2-dimethylimidazole and is found to decrease with the degree of steric hindrance provided by the 2-substituent [1]. Accordingly, the difficulty in observing a low-spin signal for 2-methylimidazole cannot arise from such a steric hindrance only. It seems likely that the stability of the low-spin bis-adduct with 2-methylimidazole at 77 K is markedly lower than at room temperature as suggested by Satterlee *et al.* [2]. The reason why the low-spin

TABLE I. Principal g-Values for Protoporphyrin IX Dimethyl Ester Iron(III) Complexes with Imidazole Derivatives in Chloroform at 77 K.

Bases ^a	pK _a (BH ⁺) ^b	Principal g-Values			References
		E _x	E _y	E _z	
<i>Hindered Imidazoles</i>					
2,4DMeIm	8.06	1.59	2.27	2.87	This work
1,2DMeIm	7.85	1.55	2.27	2.89	
2EtIm	7.70	1.55	2.26	2.92	
<i>Unhindered Imidazoles</i>					
NMeIm	7.33	1.53	2.28	2.92	7
NEtIm	7.30	1.54	2.28	2.93	7
4MeIm	7.22	1.59	2.26	2.87	This work
Im	6.65	1.68	2.28	2.80	7
Him	5.73	1.70	2.27	2.78	7
4PhIm	5.70	1.54	2.26	2.90	This work
5ClNMeIm	4.75	1.54	2.27	2.88	
NAcIm	3.6	1.49	2.22	2.96	

^a Abbreviations used: 2,4DMeIm, 2,4-dimethylimidazole; 1,2DMeIm, 1,2-dimethylimidazole; 2EtIm, 2-ethylimidazole; NMeIm, 1-methylimidazole; NEtIm, 1-ethylimidazole; 4MeIm, 4-methylimidazole; Im, imidazole; Him, histamine; 4PhIm, 4-phenylimidazole; 5ClNMeIm, 5-chloro-1-methylimidazole; NAcIm, 1-acetylimidazole. ^b A. Albert, *Phys. Methods Heterocycl. Chem.*, 1, 1 (1963). A. R. Katritzky and A. J. Boulton, Ed., *Adv. Heterocycl. Chem.*, 12, 103 (1970). Corrected for the presence of two protons in the conjugate acid (log 2) for NH imidazoles [1].

bis-adduct is destabilized especially for 2-methylimidazole remains to be clarified.

Table I shows the three g-values for low-spin signal of the complexes with imidazole derivatives in chloroform at 77 K. In the EPR spectra of the complex with unhindered imidazoles in chloroform, only the low-spin signal is distinctly observed in the molar ratio greater than 20. The g-values for low-spin signal of (deuteroporphyrin IX dimethyl ester) iron(III) complexes with various nitrogenous bases (pyrazoles, imidazoles, etc.) in dimethyl formamide at 77 K have been reported to become more anisotropic with an increase in basicity [5]. As shown in Table I, however, the g-values hardly vary with changes in basicity in the systems with imidazoles. Thus, the porphyrin iron(III) complexes with the nitrogenous bases classified into the same kind of heterocyclic compounds (in this study, imidazoles) are considered to exhibit essentially identical g-values under similar experimental conditions. In addition, the g-values are found to be independent of the degree of the above-mentioned steric interaction. This suggests that, for these systems, the energy level structure of ground Kramers doublets of iron(III) which defines the g-values [6] is not appreciably influenced by both the basicity of the axial base and the degree of steric interaction.

Experimental

The method of preparation of Fe(PPDME)Cl and the purification of imidazole derivatives were

identical with those described before [1]. Chloroform of analytical grade was purified by the usual method. Other solvents were spectro-grade and used without further purification.

The X-band EPR spectra were taken as described before [7]. Measurements were made on solutions ranging in the concentration of Fe(PPDME)Cl from 1×10^{-2} to 5×10^{-2} M and on solids. The solid sample was prepared as follows. The sample tube containing a mixture of hindered imidazole and Fe(PPDME)Cl was sealed *in vacuo*, kept at the fusion temperature of the former (160, 100, 180, 100, and 50 °C for 2-methyl-, 2-ethyl-, 2-phenyl-, 2,4-dimethyl-, and 1,2-dimethylimidazole, respectively) for 1 hr, cooled to room temperature, and then used for measurements.

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