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COMMUNICATION

THE NOVEL MAGNETIC PROPERTIES OF FERRIC ION ON THE ADDITION OF PYRIDINES TO A TAILED PORPHYRIN IRON(III) COMPLEX AS STUDIED BY EPR SPECTROSCOPY

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Abstract—The EPR spectra of the products due to the addition of pyridines to two new tailed porphyrin iron complexes, 5-[*o*-(4-(1-imidazolyl)butoxyl)phenyl]10,15,20-triphenylporphyrinatoiron(III) chloride (*o*-ImBPTPPFe^{III}Cl) and 5-[*o*-(4-(3-pyridyloxyl)butoxyl) phenyl]10,15,20-triphenylporphyrinatoiron(III) chloride (*o*-PyBPTPPFe^{III}Cl) have been investigated. The novel magnetic properties of the iron(III) ion in the pyridine-adducts of *o*-ImBPTPPFe^{III}Cl were observed at 77 K.

Recently, considerable attention has been paid to the EPR studies on magnetic properties of ferric ion in haemoprotein and its model compounds.[1] However, imidazole-appended iron porphyrins, which play an important role for our current understanding of the fundamental chemistry of haemoglobin and myoglobin oxygen bonding,[2] and the addition of low-basicity pyridines to these tailed porphyrins, have rarely been studied by EPR. Here we report the EPR studies on the addition of pyridines to 5-[*o*-(4-(1-imidazolyl)butoxyl)phenyl] 10,15,20-triphenylporphyrinatoiron(III) chloride (*o*-ImBPTPPFe^{III}Cl) and 5-[*o*-(4-(pyridyloxyl)butoxyl)phenyl]10,15,20-triphenylporphyrinatoiron(III) chloride (*o*-PyBPTPPFe^{III}Cl), and the novel magnetic properties of ferric ion on the addition of pyridines to *o*-ImBPTPPFe^{III}Cl.

o-ImBPTPPFe^{III}Cl and *o*-PyBPTPPFe^{III}Cl were prepared and identified according to the previously published method.[3] EPR samples were prepared from stock solutions of porphyrin iron(III) complexes and pyridines in choroform such that the final $[Fe^{III}] = 10^{-2}$ mol dm^{-3}, with excess pyridines in order to observe complete formation of adducts. EPR spectra were recorded at 77 K on a Varian E-115 spectrometer operating at X band; the frequency was calibrated for each sample with DPPH ($g = 2.0036$).

Adding pyridine to the chloroform solution of *o*-PyBPTPPFe^{III}Cl as well as dissolving *o*-PyBPTPPFe^{III}Cl in pyridine, we did not observe any EPR signal of the low-spin adduct, *o*-PyBPTPPFe^{III}(Py)$_2$Cl. In general, the pyridine-adducts of porphyrin iron(III) complexes gave no

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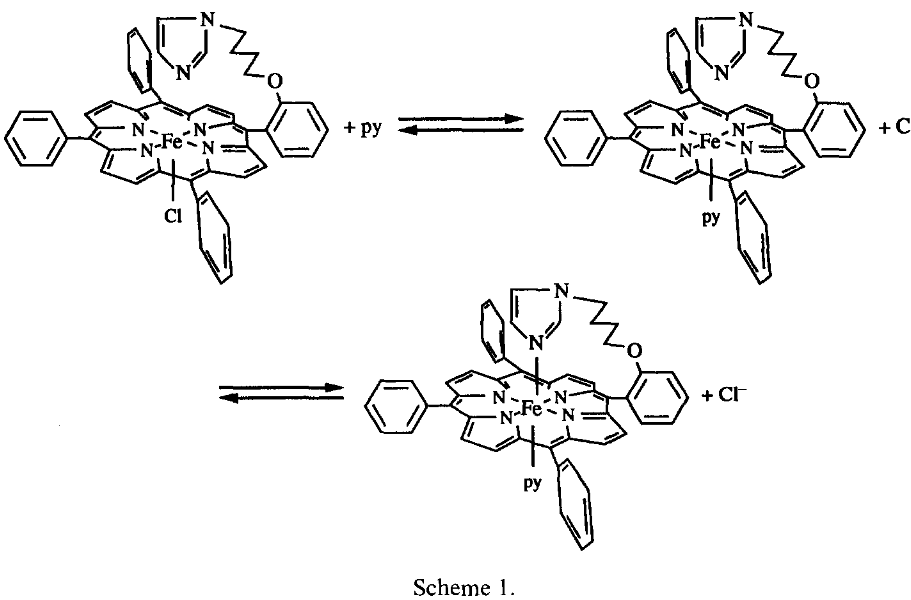
EPR signals at 77 K but below 30 K yield a strong $g_{\max} \sim 3.4$ signal observed by Migita *et al.*[4] and Palmer and co-workers.[5] It is the result of a perpendicular alignment of the two pyridine planes.[6]

Surprisingly, when pyridines were added to the choroform solution of *o*-ImBPTPPFe^{III}Cl, the novel magnetic properties of the ferric ion were observed, that is, the characteristic EPR signal of high-spin ferric ion disappeared immediately, and two kinds of EPR signals appeared (Fig. 1). The novel magnetic properties of ferric ion are quite similar to the observation for the addition of 3,4-lutidine to ImCH$_2$CH$_2$ONHTPPFe^{III}Cl reported by Walker *et al.*[7] We consider that it is the result of two kinds of species of different spin-states in the reaction equilibrium system (Scheme 1). We have reported previously that the terminal imidazole group can coordinate with ferric ion in *o*-ImBPTPPFe^{III}Cl to form a six-coordinate adduct *o*-ImBPTPPFe^{III}(Py)Cl in the presence of pyridines;[8] one kind of species is the six-coordinate porphyrin iron(III) complexes, whose anisotropism leads to three principal g values ($g_z = 3.08$, $g_y = 2.20$, $g_x = 1.27$). This result indicates that the coordination of the terminal group of the tailed porphyrin iron(III) complexes leads to the configuration change of adducts and the low-spin EPR signals observed at 77 K. The EPR signal of the other species ($g_\perp = 4.26$, $g_\parallel = 2.00$) appears to be characteristic of an admixed intermediate spin-state.[9] Generally, the coordination of the strong field ligand leads to a low-spin ($S = 1/2$) adduct, weaker field ligands lead to high-spin or intermediate ($S = 3/2$) or admixed intermediate spin-state,[10] so we conclude that this admixed intermediate-spin species is the five-coordinate intermediate species produced in the process of formation of the low-spin six-coordinate adduct, *o*-ImBPTPPFe^{III}(Py)Cl; in this case the terminal imidazole group (strong field ligand) does not coordinate with ferric ion, and only one molecule of pyridine (weak field ligand) coordinates with ferric ion (Scheme 1). Generally, it is difficult for the monopyridine adducts of porphyrin iron(III) complexes to give EPR signals at 77 K. The fact that the five-coordinate intermediate species give admixed intermediate-spin signals at 77 K is probably related to the effect of the terminal imidazole group, which affects the coordination environment of the ferric ion in a certain way.

Fig. 1. EPR spectra for: (a) *o*-ImBPTPPFe^{III}Cl, (b) *o*-ImBPTPPFe^{III}Cl + Py in choroform at 77 K.

From Table 1 it can been seen that there is a considerable difference between pyridine-adducts of *o*-ImBPTPPFe^{III}Cl and of ImCH$_2$CH$_2$OCONHTPPFe^{III}Cl. It seems that these kinds of novel magnetic properties of ferric ion are not only related to the electronic synergism between the two



Scheme 1.

Table 1. The EPR g values for ferric porphyrins and their pyridine adducts

Complexes	Bases	$g_\perp$	$g_\parallel$	g_z	g_y	g_x	T (K)
TPPFe^{III}Cl[c]	Py			[a]	[a]	[a]	77
				3.4	[b]	[b]	<30
o-PyBPTPPFe^{III}Cl		5.56	1.99				77
	Py			[a]	[a]	[a]	77
o-ImBPTPPFe^{III}Cl		5.89	2.00				77
	Py	4.26	2.00	3.08	2.20	1.27	77
	4-CH_3Py	4.26	2.00	3.04	2.20	1.32	77
	4-BenzylPy	4.27	2.00	3.05	2.21	1.33	77
	2-AcetylPy	4.28	2.00	2.90	2.30	1.47	77
$ImCH_2CH_2ONHTPPFe^{III}Cl$[c]	3,4-Lutidine			3.28	[a]	[a]	77

[a] No signal; [b] not resolved; [c] ref. 6.

unlike axial ligands, but are also influenced by the effect of the chain-linked terminal imidazole group.

EPR studies on other porphyrin iron(III) complexes with varied carbon chain-linked terminal imidazole groups are in progress.

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