Nitrosyl iron(II) complexes of porphyrins substituted with highly electron-withdrawing CF₃ groups: electronic absorption, MCD and EPR spectral study

Tetsuhiko Yoshimura*, Hotoshi Kamada

Institute for Life Support Technology, Yamagata Technopolis Foundation, Kurumanomae-683, Numagi, Yamagata 990 (Japan)

Hiroo Toi, Shinji Inaba

Department of Bioengineering, Nagaoka University of Technology, Nagaoka 940-21 (Japan)

and Hisanobu Ogoshi

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

Abstract

Five- and six-coordinated nitrosyl iron(II) complexes of etioporphyrin I and electron-deficient porphyrins with one, two or four CF₃ groups at pyrrole β-positions of a porphyrin have been prepared and the electronic absorption, MCD, IR and EPR spectra of their complexes have been measured at room temperature and 77 K. Both the line shape and parameters varied with the number of CF₃ substituents with a highly electron-withdrawing ability. Their data were evaluated by using the first redox potentials of free base porphyrin as a measure of the electron-withdrawing or -donating ability of the porphyrin peripheral substituents.

Introduction

The electronic properties of iron porphyrin complexes have been demonstrated to vary with the substitution of the porphyrin peripheral groups (*cis* effect) as well as with an exchange of one axial ligand for another or a variation of the electronic state of the axial ligands (*trans* effect) [1–5]. The introduction of a substituent to the pyrrole β-position can be expected to bring about a greater *cis*-effect than that of a substituent to the *o*, *m* or *p* position on the *meso* phenyl groups, because the former substituent can more directly participate in the porphyrin π-electron system than the latter. In preceding papers, we reported the spectral properties of iron(II) and iron(III) complexes of porphyrin substituted with CF₃ groups on pyrrole β-position(s) [6–8]. Since a CF₃ group has a highly electron-withdrawing ability, the spectral properties of the iron porphyrins with a CF₃ group change markedly with the number of CF₃ substituents. In this study, we describe the electronic absorption, magnetic circular dichroism (MCD), IR and EPR spectral properties of the nitrosyl iron(II) complexes of electron-deficient porphyrins with

one, two or four CF₃ groups at pyrrole β-positions (the dianion of the porphyrins; MTFP, BTFP and TTFP, respectively) and etioporphyrin I (EtPI).

Experimental

Fe(EtPI)Cl was obtained commercially and Fe(MTFP)Cl, Fe(BTFP)Cl and Fe(TTFP)Cl were synthesized as described before [7]. Imidazole (ImH) was recrystallized from chloroform–petroleum ether and 1-methylimidazole (*N*-MeIm), pyridine (Py) and 2,4,6-trimethylpyridine (2,4,6-Me₃Py) were stored over KOH and distilled at reduced pressure under nitrogen atmosphere. All other chemicals used were obtained as the best available grade and were used without further purification.

The electronic absorption spectra were recorded on a Hitachi U-3210 spectrometer at 23 ± 1 °C. The MCD spectra were measured at room temperature with a JASCO J-500A spectropolarimeter attached to an electromagnet (1.3 T) and a JASCO DP-501 data processor for data accumulation and manipulation. The MCD results are expressed as $\Delta\epsilon_m$ (M cm T)$^{-1}$, where 1 $T = 10\,000$ G. The IR absorption spectra of chloroform

---

*Author to whom correspondence should be addressed.

or 1-methylimidazole solutions of the complexes were measured in the region 1550–1750 cm^{-1}, using CaF$_2$ windows with a pathlength of 0.1 mm. They were recorded on a JASCO A-302 apparatus attached with a DP-A300 data processor for data accumulation and manipulation. EPR measurements were carried out on a JEOL RE-2X spectrometer with 100 kHz field modulation at 77 K. For accurate measurements of the EPR parameters, the microwave frequencies were measured with a digital frequency counter (Advantest, model TR-5211A) and the magnetic field was calibrated with an NMR field meter (Echo Electronics, EMF 2000A).

Electronic absorption, MCD, IR and EPR samples were prepared as described before [9, 10].

Results and discussion

As the numbers of electron-withdrawing CF$_3$ groups increases, the first redox potentials of free base porphyrins become more positive [7]. In the following description, the redox potentials are used as a measure of the electron-withdrawing or -donating ability of the porphyrin peripheral substituents.

Electronic absorption and MCD spectra

Table 1 lists the electronic absorption spectral data of nitrosyl(porphyrinato)iron(II) complexes with and without an axial ligand *trans* to an NO group.

In the five-coordinated nitrosyl iron(II) complexes without the axial ligand, both electronic and MCD spectra of the TTFP complex are similar to those of the EtPI complex in overall spectral pattern as shown in Figs. 1 and 2, though their absorption and MCD band maxima shift to the longer wavelength side on going from the EtPI to TTFP complex. (The splitting in the Soret region of the MCD spectrum of Fe(TTFP)(NO) (Fig. 2(b)) remains unexplained.)

Upon addition of nitrogenous bases to a five-coordinated nitrosyl iron(II) complex, the electronic spectrum gradually changes to that with the spectral pattern characteristic of the six-coordinated complex. As shown in Table 1 and Fig. 3, the solutions containing the nitrosyl iron(II) complexes of CF$_3$-substituted porphyrins and a high concentration of unhindered nitrogenous bases exhibited the electronic absorption and MCD spectra of the six-coordinated complex, while that containing the EtPI complex and a higher concentration of bases exhibited the spectra of a mixture of five- and six-coordinated complex. In the system with the TTFP complex, even 2,4,6-trimethylpyridine which is one of the highly hindered bases can coordinate to iron(II) to form a six-coordinated complex. These results indicate that the introduction of highly electron-withdrawing CF$_3$ groups to the porphyrin periphery causes the decrease in electron density on the pyrrole nitrogen and consequently an increase in the affinity of iron(II) for an axial ligand.

TABLE 1. Electronic spectral data of nitrosyl(porphyrinato)iron(II) complexes at room temperature[a]

Porphyrin	$E_{1/2}(\mathrm{I})$[b] (V)	Base	Absorption maxima (nm) (ϵ (mM^{-1} cm^{-1}))				
			Soret			β	α
			5-coord.[c]	6-coord.[d]	5-coord.[e]	5,6-coord.	5,6-coord.
EtPI	−1.39	none[f]	388.4(90.3)		480.4(10.7)	530.0(11.1)	555.2(10.7)
		N-MeIm	390sh(81.3)	406.4(97.9)	477.2(9.78)	534.0(12.0)	558.4(11.3)
		N-MeIm[g]		407.2(130)	480sh(8.4)	534.0(12.0)	560.8(10.7)
		ImH	390.0(95.3)		476.8(14.1)	527.6(11.9)	558.4(11.4)
		Py	394.4(86.1)		480.0(9.92)	532.8(11.0)	558.8(11.0)
		2,4,6-Me$_3$Py	390.0(92.1)		480.0(12.0)	530.4(11.4)	559.2(11.3)
MTFP	−1.22	*N*-MeIm		410.0(122)		540.0(11.8)	576.4(10.8)
		Py		408.4(120)	472sh(9.3)	541.6(11.1)	577.2(10.3)
BTFP	−1.08	*N*-MeIm		414.0(150)		543.6(11.9)	578.8(8.25)
		Py		411.6(133)		543.2(11.5)	573sh(8.7)
TTFP	−0.81	none[f]	394.4(89.6)		465sh(14)	542.8(9.92)	565sh(9.4)
		N-MeIm[h]		416.0(156)		542.4(11.6)	571.0(6.9)
		ImH		415.6(169)		543.2(13.1)	570sh(7.5)
		Py		414.0(182)		542.4(12.3)	568sh(8.1)
		2,4,6-Me$_3$Py	398.8(90.6)	408.0(92.9)	472sh(14)	542.8(12.6)	568sh(10.7)

[a]Solvent, CHCl$_3$; [Fe(P)(NO)] = 0.013–0.018 mM; [*N*-MeIm] = 2.4 M, [ImH] = 0.23 M, [Py] = 4.0 M, [2,4,6-Me$_3$Py] = 4.0 M; unless otherwise stated. [b]The first redox potentials of free base porphyrins; ref. 7. [c]Soret-band maxima of five-coordinated complexes. [d]Soret-band maxima of six-coordinated complexes. [e]Absorption band observed only in five-coordinated complexes. [f]Solvent: CH$_2$Cl$_2$. [g][*N*-MeIm] = 4.8 M. [h][*N*-MeIm] = 1.2 M.
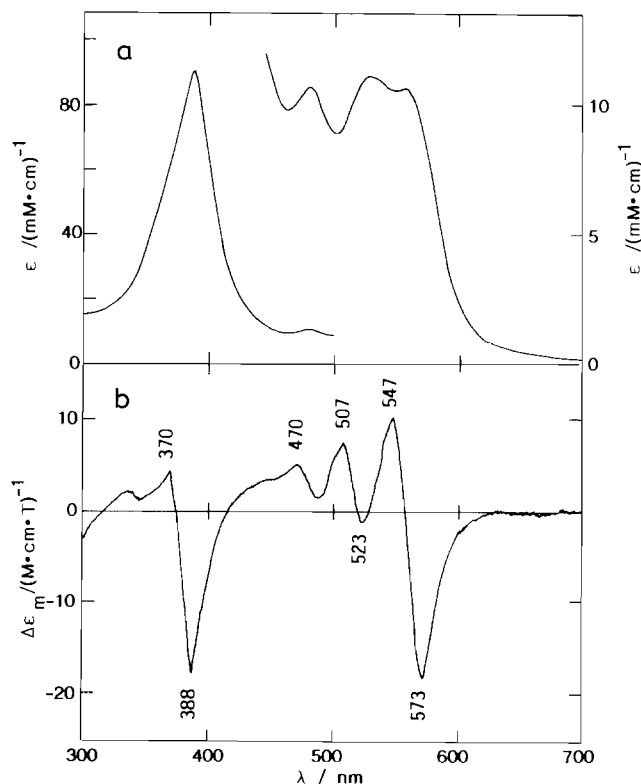
Fig. 1. Electronic (a) and MCD (b) spectra of Fe(EtPI)(NO) in dichloromethane at room temperature. [Fe(EtPI)(NO)] = 0.0174 mM.

As the electron-withdrawing ability of porphyrinato ligand increases, the absorption band maxima of the six-coordinated complexes shift to the longer wavelength side similar to those of the five-coordinated complex (Table 1), which has been observed in the electronic absorption spectra of *meso* unsubstituted porphyrins and their metal complexes [11].

The ratio of absorption intensity, $\epsilon(\alpha)/\epsilon(\beta)$, decreases from the six-coordinated MTFP complex to the BTFP complex and to the TTFP complex (Table 1, Fig. 3). Such a decrease in the ratio has been observed in the series of the free base porphyrin of MTFP to BTFP and to TTFP and their iron(II) complexes with bis 1-methylimidazole [8]. This decrease which is accompanied by the increase of porphyrin peripheral substituents in electron-withdrawing ability can result from the decrease of the splitting in the HOMOs (a_{1u} and a_{2u}) as pointed out by Spellane *et al*. [12]. Thus the introduction of highly electron-withdrawing CF_3 groups to pyrrole β-positions leads to considerable perturbation of the porphyrin π-electron system.

The spectral pattern of the MCD spectrum of Fe(TTFP)(NO)(N-MeIm) (Fig. 3) which contains low-spin iron(II) resembles that of the low-spin iron(III) complex of TTFP ([Fe(TTFP)(ImH)$_2$]$^+$) [7] rather than that of low-spin iron(II) complex of TTFP
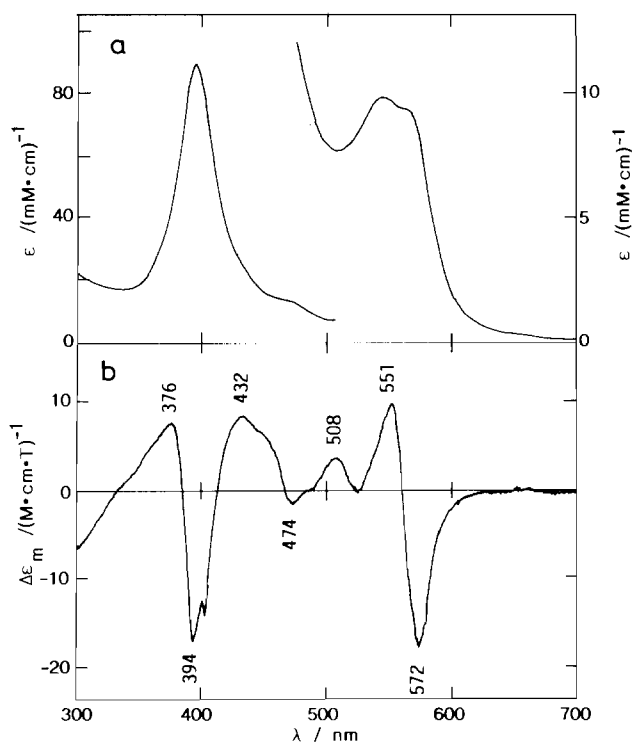

Fig. 2. Electronic (a) and MCD (b) spectra of Fe(TTFP)(NO) in dichloromethane at room temperature. [Fe(TTFP)(NO)] = 0.0167 mM.

TABLE 2. NO stretching frequencies of five-coordinated nitrosyl(porphyrinato)iron(II) complexes and six-coordinated complexes with 1-methylimidazole at room temperature

Porphyrin	$E_{1/2}(I)^a$ (V)	Five-coordinates[b]	Six-coordinates[c]
EtPI	−1.39	1670	1612
TTFP	−0.81	1702	1648

[a]See footnote b of Table 1. [b]Solvent: chloroform. [c]Solvent: 1-methylimidazole.

(Fe(TTFP)(N-MeIm)$_2$) [8], though the MCD intensity of the Soret-band region is much weaker than that of the low-spin iron(III) complex. This suggests that the charge of iron and NO in the Fe(TTFP)(NO)(N-MeIm) is $Fe^{2+\delta}$ and $NO^{\delta-}$, respectively.

NO stretching frequencies

Table 2 lists the NO stretching frequencies (ν_{NO}) of nitrosyl iron(II) complexes of EtPI and TTFP in chloroform and in 1-methylimidazole. The ν_{NO} values in chloroform and in 1-methylimidazole correspond to those of five-coordinate complexes without an axial ligand and six-coordinate complexes with 1-methylimidazole as an axial ligand, respectively.

The ν_{NO} of Fe(EtPI)(NO) and Fe(EtPI)(NO)(N-MeIm) were slightly lower than those of

TABLE 3. EPR parameters of five-coordinated nitrosyl(porphyrinato)iron(II) complexes in toluene at room temperature and 77 K

| | Porphyrin | $E_{1/2}(I)^a$ (V) | At room temperature | | At 77 K | | | | | | | | |
			g_{iso}	A_{iso} (G)	g values					Hyperfine coupling constant			
					g_1	$g_?$	$g_{2'}$	g_2	g_3	A_1 (G)	$A_?$ (G)	A_2 (G)	A_3 (G)
^{14}NO	EtPI	−1.39	2.0520	16.17	2.107	2.060	2.037	2.024	2.0103	14.6	14.9	19.2	16.9
	TTFP	−0.81	2.0564	16.69	2.109	2.064	2.038	2.026	2.0104	15.0	21.6	19.5	17.3
^{15}NO	EtPI	−1.39	2.0518	23.11	2.106	2.060	2.033	2.024	2.0102	21.1	20.0	26.2	23.0
	TTFP	−0.81	2.0563	24.31	2.108	2.063	2.035	2.026	2.0104	22.2	23.8	26.9	23.9

[a]See footnote b of Table 1.
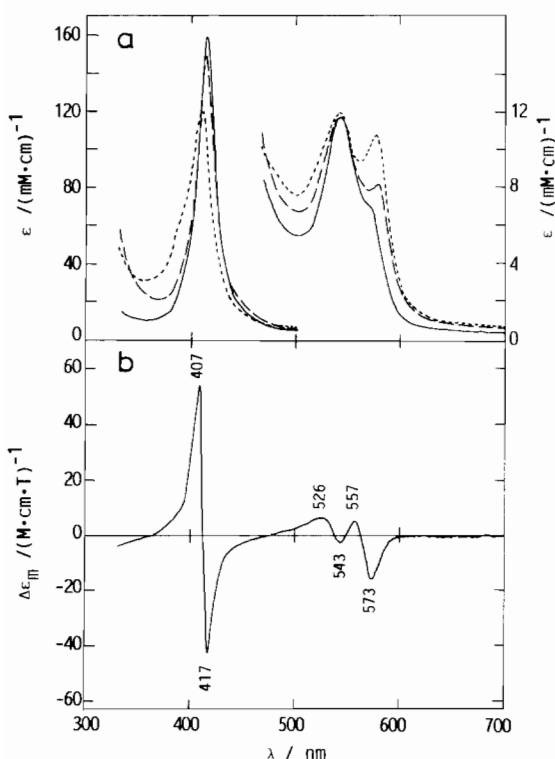
Fig. 3. Electronic (a) and MCD (b) spectra in chloroform at room temperature. Dotted line, Fe(MTFP)(NO)(N-MeIm) (0.0132 mM); dashed line, Fe(BTFP)(NO)(N-MeIm) (0.0145 mM); solid line, Fe(TTFP)(NO)(N-MeIm) (0.0156 mM).

TABLE 4. EPR parameters of six-coordinated nitrosyl-(porphyrinato)iron(II) complexes with 1-methylimidazole and pyridine in toluene at room temperature

Porphyrin	$E_{1/2}(I)^a$ (V)	g_{iso}	
		N-MeIm	Py
EtPI	−1.39	2.022	2.0371
MTFP	−1.22	2.020	2.0353
BTFP	−1.08	2.016	2.0302
TTFP	−0.81	2.012	2.0247

[a]See footnote b of Table 1.

Fe(PPIXDME)(NO) and Fe(PPIXDME)(NO)(N-MeIm) (1675 and 1618 cm^{-1}) [13]. The ν_{NO} of both five- and six-coordinated complexes of TTFP were markedly higher than those of EtPI. This ν_{NO} change can be explained in the same manner as that on nitrosyl iron(II) complexes with tetrakis(p-substituted phenyl)porphyrin ((p-X)TPP) [10]. As the electron-withdrawing ability of the porphyrin peripheral substituents increases, the iron-to-NO π backbonding is weakened and thus the electron density of iron d_π and NO π^* orbitals decreases, followed by an observed increase in ν_{NO}. The changes in ν_{NO} per unit volt in $E_{1/2}(I)$ of free base porphyrins (55 cm^{-1} in the five- and 62 cm^{-1} in the six-coordinated complexes) are comparable to those for nitrosyl iron(II) complexes with (p-X)TPP (71 and 70 cm^{-1}, respectively) [10].

EPR spectra: five-coordinated complexes

Table 3 lists the EPR parameters of five-coordinated Fe(EtPI)(NO) and Fe(TTFP)(NO) at room temperature and at 77 K, together with the first redox potential of free base porphyrins. All the parameters were determined on the basis of the definition previously described [10]. Those of Fe(TTFP)(NO) were larger than those of Fe(EtPI)(NO), which can be explained as a result of the introduction of highly electron-withdrawing CF_3 group to the four pyrrole β-positions. The spin density on the nitrogen of NO was estimated to be about 3% from three hyperfine coupling constants at 77 K according to the method of McNeil et al. [14]. This suggests that the unpaired electron of an NO group largely delocalizes toward the iron d_{z^2} orbital.

As described in the section 'NO Stretching Frequencies', the electron density on the iron d_π and NO π^* orbitals decreases on introduction of an electron-withdrawing CF_3 group to the pyrrole position, followed by a shift of the unpaired electron on the d_{z^2} orbital toward NO nitrogen. The slight increase of the spin

TABLE 5. EPR parameters of six-coordinated nitrosyl(porphyrinato)iron(II) complexes with 1-methylimidazole in toluene at 77 K

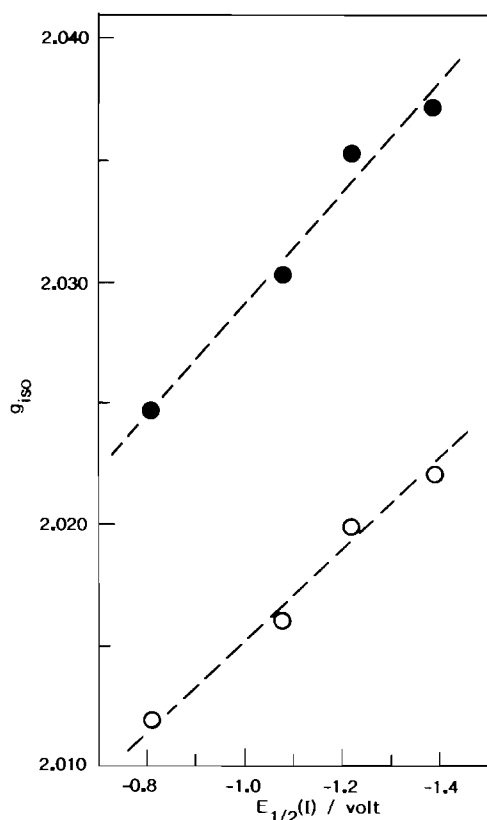|	Porphyrin	$E_{1/2}(I)^a$ (V)	g values					Hyperfine coupling constant	
			g_1	g_{II-1}	g_2	g_3	$g_{3'}$	A_2 (G)	a_2 (G)
^{14}NO	EtPI	−1.39	2.072	2.037	2.0041	1.968	1.976	22.2	6.90
	MTFP	−1.22	2.071	2.035	2.0036	1.966	1.973	22.3	6.90
	BTFP	−1.08	2.070	2.035	2.0034	1.965	1.972	22.6	6.96
	TTFP	−0.81	2.067	2.030	2.0025	1.962	1.971	23.4	7.15
^{15}NO	EtPI	−1.39	2.073	2.034	2.0044	1.971	1.976	30.3	6.80
	TTFP	−0.81	2.065	2.030	2.0028	1.966	1.972	32.6	7.06

^{a}See footnote b of Table 1.

Fig. 4. Relationship between the g_{iso} values (at room temperature) of six-coordinated nitrosyl iron(II) complexes with a base and the $E_{1/2}(I)$ values of free base porphyrin. Base: O, 1-methylimidazole; ●, Py. The trend in the data is indicated by the dashed line.

Fig. 5. Relationship between the g_1 and g_3 values (at 77 K) of six-coordinated nitrosyl iron(II) complexes with a base and the $E_{1/2}(I)$ values of free base porphyrin. Base: O, 1-methylimidazole; ●, Py. The trend in the data is indicated by the dashed line.

density on the NO nitrogen and the stabilization of the d_{z^2} orbital can lead to an increase in the hyperfine coupling constants and the g values.

EPR spectra: six-coordinated complexes

Tables 4 and 5 list the EPR parameters of six-coordinated nitrosyl iron(II) complexes with 1-methylimidazole and pyridine as an axial ligand *trans* to NO group at room temperature and at 77 K, together with
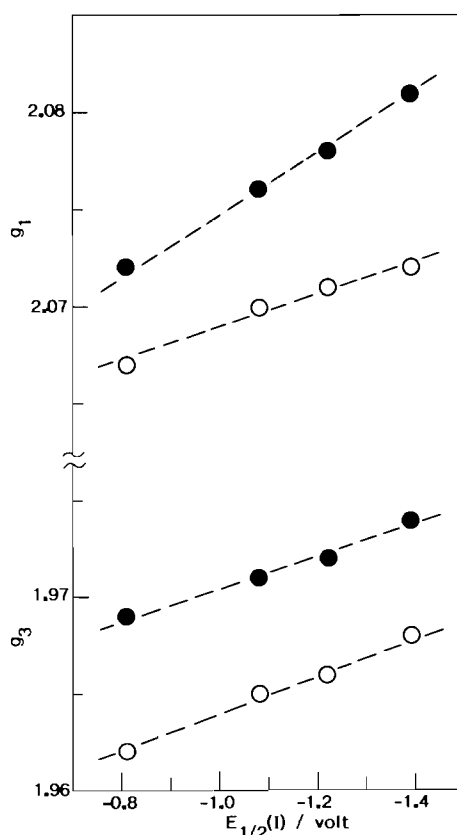
the first redox potential of free base porphyrins. (The data of the pyridine complexes at 77 K are shown in Figs. 5 and 6.) All the parameters were determined on the basis of the definition previously described [10].

Figures 4–7 illustrate the $E_{1/2}(I)$ dependence of the g values and hyperfine coupling constants of six-coordinated nitrosyl iron(II) complexes. As the electron deficiency of porphyrin increases, these g values in the six-coordinated complexes decrease and the g_{iso} value and $(g_1 + g_2 + g_3)/3$ values approach the free spin value,
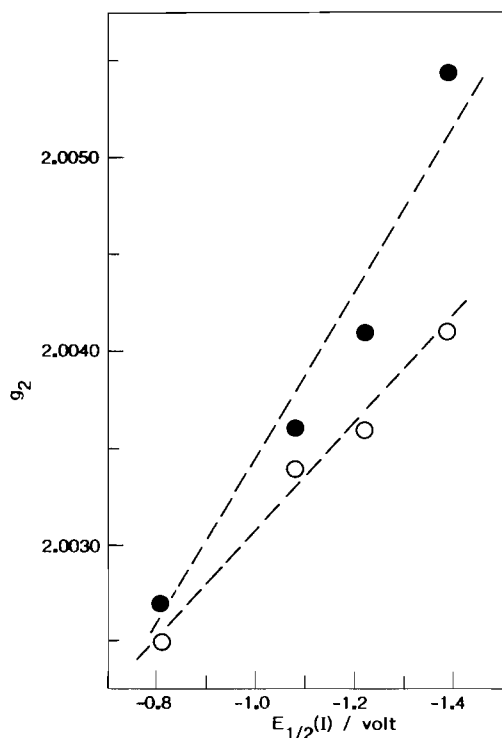
Fig. 6. Relationship between the g_2 values (at 77 K) of six-coordinated nitrosyl iron(II) complexes with a base and the $E_{1/2}(I)$ values of free base porphyrin. Base: O, 1-methylimidazole; ●, Py. The trend in the data is indicated by the dashed line.
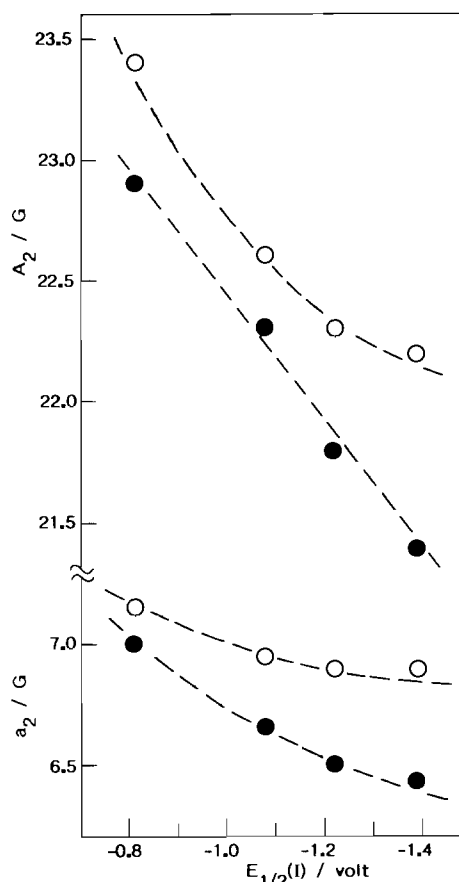

Fig. 7. Relationship between the A_2 and a_2 values (at 77 K) of six-coordinated nitrosyl iron(II) complexes with a base and the $E_{1/2}(I)$ values of free base porphyrin. Base: O, 1-methylimidazole; ●, Py. The trend in the data is indicated by the dashed line.

while the g value in the five-coordinated complexes increase as described above. As shown in Fig. 7, A_2 and a_2 values increase as the electron deficiency increases in a similar way to the case of the five-coordinated complexes.

As described above, an increase in the electron-withdrawing ability of the porphyrin periphery results in a decrease in the electron density on the iron d_π and NO π^* orbitals, followed by a shift of the unpaired electron on the d_{z^2} orbital toward the NO nitrogen. The increase in the unpaired electron density on the NO nitrogen leads to an increase in hyperfine coupling constants. The decrease in the electronic density on the iron d orbital can be compensated by electron donation from the axial ligand (1-methylimidazole or pyridine) trans to the NO group through the d_{z^2} orbital. The resulting destabilization of the d_{z^2} orbital can induce the observed decrease in the g_{iso} and $(g_1+g_2+g_3)/3$ values toward the free spin value.

In a preceding paper [10], we reported the dependences of the ν_{NO}, g values and hyperfine coupling constants of five- and six-coordinated nitrosyl iron(II) complexes of a series of tetrakis(p-substituted phenyl)porphyrins ((p-X)TPP) on the redox potentials ($E_{1/2}(I)$) of the free base porphyrins. The $E_{1/2}(I)$ of (p-X)TPP and CF$_3$-substituted porphyrins were measured employing the reference electrode of Ag/AgNO$_3$ [15]

and Ag/AgCl [7] and the solvent of dimethyl formamide and dichloromethane, respectively. On considering the differences of the conditions used for the measurement of the potentials, the $E_{1/2}(I)$ dependences obtained for the nitrosyl iron(II) complexes of CF$_3$-porphyrins described above seem to be almost similar to those for the complexes of (p-X)TPP.

Acknowledgements

References

1 W. S. Caughey, in G. L. Eichhorn (ed.), Inorganic Chemistry, Vol. 2, Elsevier, Amsterdam, 1973, pp. 797–831.

2 J. W. Buchler, W. Kokisch and P. D. Smith, *Struct. Bonding (Berlin), 34* (1978) 79; J. W. Buchler, in D. Dolphin (ed.), *The Porphyrins*, Vol. I, Academic Press, New York, 1978, pp. 389–483.

3 (a) F. A. Walker, I. A. Barry, V. L. Balke, G. McDermott, M. Z. Wu and P. F. Linde, *Adv. Chem. Ser., 201* (1982) 377; (b) F. A. Walker, D. Reis and V. L. Balke, *J. Am. Chem. Soc., 106* (1984) 6888; (c) V. L. Balke, F. A. Walker and J. T. West, *J. Am. Chem. Soc., 107* (1985) 1226.

4 (a) K. M. Kadish, in A. B. P. Lever and H. B. Gray (eds.), *Iron Porphyrins*, Part II, Addison-Wesley, Reading, MA, 1983, pp. 161–249; (b) K. M. Kadish, *Prog. Inorg. Chem., 34* (1986) 435.

5 C. E. Castro, in D. Dolphin (ed.), *The Porphyrins*, Vol. V, Academic Press, New York, 1978, pp. 1–27.

6 H. Toi, M. Honnma, A. Suzuki and H. Ogoshi, *J. Chem. Soc., Chem. Commun.,* (1985) 1791.

7 T. Yoshimura, H. Toi, S. Inaba and H. Ogoshi, *Inorg. Chem., 30* (1991) 4315–4321.

8 T. Yoshimura, H. Toi, S. Inaba and H. Ogoshi, *Bull. Chem. Soc. Jpn., 65* (1992) 1915–1919.

9 T. Yoshimura, *Bull. Chem. Soc. Jpn., 63* (1990) 3689–3691.

10 T. Yoshimura, *Bull. Chem. Soc. Jpn., 64* (1991) 2819–2828.

11 J. E. Falk, *Porphyrins and Metalloporphyrins,* Elsevier, Amsterdam, 1964.

12 P. C. Spellane, M. Gouterman, A. Antipas and Y. C. Liu, *Inorg. Chem., 19* (1980) 386.

13 T. Yoshimura, *Arch. Biochem. Biophys., 220* (1983) 167.

14 D. A. C. McNeil, J. B. Raynor and M. C. R. Symmons, *J. Chem. Soc.,* (1965) 410.

15 P. Worthington, P. Hambright, R. E. X. Williams, J. Reid, C. Burnham, A. Shamin, J. Turay, D. M. Bell, R. Kirkland, R. G. Little, N. Datta-Gupta and U. Eisner, *J. Inorg. Biochem., 12* (1980) 281.