

## Determination of the Field Strengths of Weak Neutral Ligands Having Oxygen as Coordination Atom

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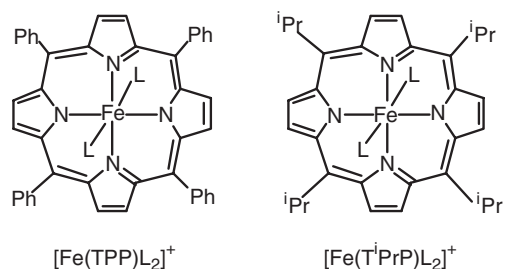
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Weakness of various neutral ligands having oxygen as coordination atom was ranked on the basis of the pyrrole proton chemical shifts of planar  $[\text{Fe}(\text{TPP})\text{L}_2]^+$ . Furthermore, weakness of the ligands, which is difficult to determine from the NMR data of planar  $[\text{Fe}(\text{TPP})\text{L}_2]^+$ , was successfully differentiated by the use of highly ruffled  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ . Among the 10 ligands examined, THF turned out to be the weakest ligand.

Oxygen-containing neutral compounds can coordinate various metal ions and regulate the physicochemical properties of a wide variety of synthetic complexes as well as naturally occurring metalloenzymes. In general, the field strength of these ligands is difficult to be determined because of their weak coordination ability. Several years ago, Reed and Guiset ranked the ligand field strength of weakly binding anion (X) on the basis of the magnetic properties of  $[\text{Fe}(\text{TPP})\text{X}]$  and called the hierarchy as magnetochemical series.<sup>1,2</sup> We have applied this method to determine the weakness of neutral ligands having oxygen as coordination atom.

The  $\text{CD}_2\text{Cl}_2$  solution of oxygen-containing neutral ligand (L) was added to  $[\text{Fe}(\text{TPP})]\text{ClO}_4$  placed in an NMR sample tube. In each case, the pyrrole-H signal shifted downfield and approached to the constant value, which was taken as the pyrrole-H chemical shift of  $[\text{Fe}(\text{TPP})\text{L}_2]^+$ . Table 1 lists the chemical shifts of the pyrrole and phenyl protons of all the complexes examined in this study. Figure 1 shows the Curie plots of the pyrrole signals of some selected complexes.



The chemical shift of the pyrrole-H is known to be a good probe to determine the spin state of iron(III) porphyrin complexes.<sup>3</sup> The high-spin ( $S = 5/2$ ) complexes always show the pyrrole signal fairly downfield because of the presence of the unpaired electron in the  $d_{x^2-y^2}$  orbital. Thus, the complexes **1a–6a** are in a quite pure high-spin state because the pyrrole signals of these complexes appeared at 67.2–73.2 ppm.<sup>4,5</sup> The high-spin state of these complexes was also confirmed by the EPR spectra taken in frozen  $\text{CH}_2\text{Cl}_2$  solution at 4.2 K; the  $g_{\perp}$  and  $g_{\parallel}$  values of **4a** were 5.95 and 2.00, respectively. In contrast, the intermediate-spin ( $S = 3/2$ ) complexes show the pyrrole signal fairly upfield because the  $d_{x^2-y^2}$  orbital has no unpaired electron and also

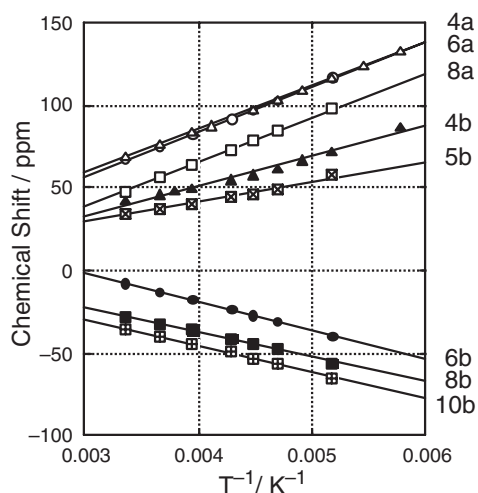
**Table 1.** <sup>1</sup>H NMR Chemical Shifts ( $\text{CD}_2\text{Cl}_2$ , 298 K,  $\delta$  ppm)

Entries	Ligands (L)	Pyrrole	<i>o</i> ( $\text{H}_{\alpha}$ )	<i>m</i> ( $\text{H}_{\beta}$ )	<i>p</i>	Int /%
a) $\text{Fe}(\text{TPP})\text{L}_2^+$						
1a	$\text{Ph}_3\text{PO}$	73.2	12.3	9.4	9.6	0
2a	3,5-Me <sub>2</sub> PyNO	71.0	12.8	9.4	9.7	2
3a	4-MePyNO	70.7	12.7	9.4	9.7	2
4a	PyNO	68.9	13.3	9.5	9.8	4
5a	4-ClPyNO	67.2	13.2	9.7	9.9	6
6a	DMSO	67.2	13.0	9.6	9.7	6
7a	DMF	60.2	13.5	9.9	9.9	12
8a	$\text{CH}_3\text{OH}$	48.1	13.8	10.1	10.0	23
9a	$\text{Et}_2\text{N-NO}$	33.1	14.1	10.0	10.1	37
10a	THF	3.1	14.1	10.1	10.3	64
b) $\text{Fe}(\text{T}^i\text{PrP})\text{L}_2^+$						
1b	$\text{Ph}_3\text{PO}$	37.2	(12.9)	(6.1)	—	33
2b	3,5-Me <sub>2</sub> PyNO	57.6	(10.9)	(6.3)	—	14
3b	4-MePyNO	58.5	(10.8)	(6.2)	—	14
4b	PyNO	41.7	(9.9)	(6.1)	—	30
5b	4-ClPyNO	35.2	(10.7)	(5.8)	—	35
6b	DMSO	-7.7	(8.0)	(4.6)	—	74
7b	DMF	-21.5	(7.3)	(4.2)	—	87
8b	$\text{CH}_3\text{OH}$	-28.3	(7.3)	n.d.	—	93
9b	$\text{Et}_2\text{N-NO}$	-33.9	(9.6)	(3.8)	—	99
10b	THF	-35.5	(5.7)	n.d.	—	100

n.d.: not determined.

because the  $d_{\pi}$  orbital maintains the unpaired electron. The unpaired electron in the  $d_{\pi}$  orbital delocalizes to the  $\beta$ -pyrrole carbon atoms by the iron ( $d_{\pi}$ )–porphyrin ( $3e_g$ ) interaction and induces the upfield shift of the pyrrole-H signal by the spin polarization mechanism. The data in Table 1 clearly indicate that the bis(thf) complex **10a** has the largest  $S = 3/2$  character among the  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  complexes, which indicates that the field strength of THF is much weaker than any other ligands examined in this study. It is difficult, however, to rank the field strengths of the ligands in **1a–6a** because these complexes exhibit the pyrrole signals at nearly the same positions. Thus, TPP is not a suitable porphyrin to differentiate the field strengths of these ligands.

In the previous papers, we and others have reported that the deformation of the porphyrin core stabilizes the  $S = 3/2$  spin state.<sup>6</sup> This is because, the deformation always contracts the Fe–N<sub>P</sub> bonds and raises the energy level of the  $d_{x^2-y^2}$  orbital.<sup>7</sup> Thus, highly ruffled complexes with weak axial ligands such as **10b** adopt an essentially pure  $S = 3/2$  spin state;<sup>6a</sup> the average Fe–N<sub>P</sub> bonds in nearly planar **10a** and highly ruffled **10b** are reported to be 2.016 and 1.967 Å, respectively.<sup>8,9</sup> We have



**Figure 1.** Curie plots of the pyrrole signals of  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  and  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ . Each line is signified by the entry number given in Table 1.

then expected that the  $S = 3/2$  character should increase on going from  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  to  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ . Consequently, the chemical shifts of the pyrrole-H in  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$  could be different even among the complexes **1b–6b**. Table 1 also lists the chemical shifts of the pyrrole, methine ( $\text{H}_\alpha$ ), and methyl ( $\text{H}_\beta$ ) protons of a series of  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ . As expected, the pyrrole signals of **1b–6b** shifted upfield in a different degree; they appeared at 37.2, 57.6, 58.5, 41.7, 35.2, and  $-7.7$  ppm, respectively. The reversal of the order was observed in **1b**, which should be ascribed to the steric repulsion between the  $\text{Ph}_3\text{PO}$  ligand and the *meso*-isopropyl groups; the repulsion weakens the coordination of  $\text{Ph}_3\text{PO}$ . Thus, the field strength of the ligands, which was difficult to determine in  $[\text{Fe}(\text{TPP})\text{L}_2]^+$ , is now ranked as given below:

$3,5\text{-Me}_2\text{PyNO} \approx 4\text{-MePyNO} > \text{PyNO} > 4\text{-ClPyNO} > \text{DMSO}$ .

By measuring the chemical shifts of the pyrrole signals in both  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  and  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ , we have determined the relative field strengths of a wide variety of oxygen-containing ligands and arranged them in Table 1 in descending order. Clearly, the ligands with formally charged oxygen atom such as  $\text{Ph}_3\text{PO}$  and  $\text{PyNO}$  are stronger than those with uncharged oxygen such as THF. Substituent effect on the field strengths is also seen in the substituted pyridine *N*-oxides. If we assume that the chemical shifts of the pyrrole signals in the pure intermediate- and high-spin complexes are  $-35.5$  and  $+73.2$  ppm, respectively, then the contribution of the  $S = 3/2$  spin state, Int (%), can be estimated by Eq 1, where  $\delta_L$  is the chemical shift of the pyrrole signal in  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  or  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ .<sup>10</sup> The Int (%) values determined by Eq 1 are also listed in Table 1.

$$\text{Int} (\%) = [(73.2 - \delta_L)/108.7] \times 100 \quad (1)$$

In conclusion, we were able to rank the weakness of oxygen containing ligands on the basis of the pyrrole proton chemical shifts of the planar  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  and highly ruffled  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$  complexes.

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#### References and Notes

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- Abbreviation: TPP and  $\text{T}^i\text{PrP}$ , dianions of 5,10,15,20-tetra-phenylporphyrin and 5,10,15,20-tetra-isopropylporphyrin.  $\text{Ph}_3\text{PO}$ , 3,5- $\text{Me}_2\text{PyNO}$ , 4- $\text{MePyNO}$ ,  $\text{PyNO}$ , and 4- $\text{ClPyNO}$ : triphenylphosphine oxide, 3,5-dimethylpyridine *N*-oxide, 4-methylpyridine *N*-oxide, pyridine *N*-oxide, and 4-chloropyridine *N*-oxide.
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- Strictly speaking, the Int (%) values of  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  and  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$  should be estimated independently. This is because, the chemical shifts of the pyrrole signals in the pure  $S = 5/2$  and  $S = 3/2$  complexes should be different between  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  and  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$ . Because there is no example of  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  and  $[\text{Fe}(\text{T}^i\text{PrP})\text{L}_2]^+$  showing an essentially pure  $S = 3/2$  and  $S = 5/2$ , respectively, we have applied Eq 1 to both types of complexes. Since the chemical shift of the pyrrole signal in analogous  $[\text{Fe}(\text{ArP})\text{-(THF)}_2]^+$  ( $\text{Ar} = 2,4,6\text{-trimethoxyphenyl}$ ), which is reported to adopt a quite pure intermediate-spin state, is  $-28.0$  ppm in  $\text{CDCl}_3$  at 302 K,<sup>11</sup> the Int (%) values of  $[\text{Fe}(\text{TPP})\text{L}_2]^+$  listed in Table 1 could be slightly underestimated.
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