which binding and activation of substrates (N_2, H^+, C_2H_2) cannot involve any metal but Fe. It remains to be discovered if heterometals (V, Mo) execute a binding and/or activating function in their nitrogenases.

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O_2 and CO Binding to "Jellyfish" Type Iron(II) Porphyrins

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The syntheses of "jellyfish" type iron(II) porphyrins and their O_2 and CO affinities in the presence of an excess axial base (1,2-dimethylimidazole) in toluene are reported, together with the O_2 affinities for the corresponding cobalt(II) porphyrins. The O_2 affinities for the Co(II) porphyrins decreased with an increase in the steric bulk of the fences appended to the porphyrin plane, on which the axial base binding occurs. On the other hand, the O_2 and CO affinities for the Fe(II) porphyrins did not exhibit a trend similar to that observed for the O_2 affinities for the Co(II) porphyrins. From the measurements of ^1H NMR spectra for both O_2 and CO adducts of the Fe(II) porphyrins, the conformations of cavities were significantly different in the Fe(II) porphyrin having pivalamide groups as fences, though the ^1H NMR signals of protons in the cavities were similar among the corresponding free-base porphyrins. Thus, steric effects of the cavities are responsible for the reduced O_2 and CO affinities of the Fe(II) porphyrin. Electronic paramagnetic resonance (EPR) spectra for the bisligated Fe(III) porphyrins were measured in $CDCl_3$ at 77 K, and the changes in the crystal field parameters are also discussed.

In the preceding paper,[1] we reported that O_2 affinities of "jellyfish" type Co(II) porphyrins vary with changes in the fence structures around the axial base binding site, while the cavity structures around the O_2 binding site remain unchanged (Figure 1). To explain these results, we postulated that the structural changes around the axial base induce variations in the orientation (ϕ) of the axial base plane with respect to a N(porphyrin)–Co–N(porphyrin) axis. Hence, it follows that changes in the strength of the π-electron interaction between the axial base and cobalt(II) will result in changes in O_2 affinities.

In order to elucidate on the mechanism of the changes in O_2 affinities for jellyfish porphyrinato Co(II) and Fe(II) complexes, this paper describes the syntheses of jellyfish iron(II) porphyrins and reports their O_2 and CO affinities, together with the O_2 affinities for the corresponding Co(II) porphyrins. ^1H NMR spectra for the O_2 and CO adducts of Fe(II) porphyrins were also measured to examine the environments near O_2 and CO binding sites (cavities) of these complexes. In order to obtain data on the changes in ϕ of jellyfish Fe(II) porphyrins, EPR spectra of their Fe(III) complexes were measured in the presence of excess 1-methylimidazole (1-MeIm) in frozen $CDCl_3$, and the changes in ϕ are discussed on the basis of the differences in the crystal field parameters.[2]

Experimental Section

General Information. Electronic spectra were recorded on a Hitachi 340 spectrophotometer. Affinities of O_2 and CO were determined by spectrophotometric titration using the flow method.[3] Affinities of O_2 for Co(II) porphyrins were determined as previously described.[1,4] The Fe(II) porphyrins were prepared by mixing[5] Fe(III) porphyrins in toluene with aqueous sodium dithionite under Ar. After separation of the two phases, the toluene layer was transferred under Ar into a cell mounted with a rubber septum equipped with gas-inlet and -outlet tubes. A excess amount of 1,2-dimethylimidazole (1,2-Me_2Im) was added to the solution under Ar, and various partial pressures of O_2 or CO were passed through the solution via the gas-inlet and -outlet tubes. Temperatures of the solutions were maintained at 25 ± 0.1 °C by the use of a constant-temperature circulation pump (Neslab Model RTE-8) and a variable-temperature cell holder (Hitachi). Various partial pressures of O_2 or CO were obtained by a Gas Mixture instrument (Kofloc Model GM-3A) constructed of mass flow controllers and flowmeters. The concentration of 1,2-Me_2Im was 0.07 M, while concentrations of Fe(II) porphyrins and Co(II) porphyrins were ca. 1×10^{-5} and ca. 5×10^{-5} M, respectively. The spectra were recorded in the 600–460-nm range for Co(II) porphyrins and in the 500–350-nm range for Fe(II) porphyrins. $P_{1/2}$ values (half-saturation gas pressures for O_2 or CO binding) were calculated by using the method of Beugelsdijk and Drago.[6] Reversibility was checked after the last CO or O_2 addition by purging with N_2 gas (7 mL/min) for 30 min; more than 90% reversibility was achieved after 2 h of carbonylation for the Fe(II) porphyrins and oxygenation for the Co(II) porphyrins. The reversibilities achieved after 2 h of oxygenation were more than 75%, 80%, and 90% for [Fe(Az-piv$\beta\beta$)], [Fe(Az-val$\beta\beta$)], and [Fe(Az-P)], respectively.

EPR spectra were recorded at 77 K on a JEOL FE2XG instrument operating at the X band. The magnetic field was calibrated with a NMR gaussmeter (JEOL ES-FC4), and the frequency was calibrated with MnO_2 ($g = 2.0034$). Concentrations of EPR samples were ca. 5×10^{-5} M for Fe(III) porphyrins in $CDCl_3$.

Proton NMR spectra were recorded on a JEOL GSX-400 and a JEOL FX-100 spectrometer. Preparations of NMR samples were as follows: The Fe(III) porphyrin was reduced in aqueous sodium dithionite and CH_2Cl_2 under Ar; the dichloromethane layer was washed with degassed H_2O and the solvent stripped off by passing Ar; the reduced product was dissolved in degassed toluene-d_8 containing 1,2-Me_2Im, and the solution was transferred to an NMR tube via a stainless steel tube; the solution was exposed to an atmosphere of O_2 or CO at room temperature; spectra for the O_2 and CO adducts were obtained at −20 and 24 °C, respectively; concentrations of the Fe(II) porphyrins and 1,2-Me_2Im were ca. 5×10^{-3} and 0.07 M, respectively.

Materials. Toluene was stirred with concentrated H_2SO_4 and then washed with 5% NaOH and H_2O, dried over $CaCl_2$, and distilled. 1-MeIm and 1,2-Me_2Im were vacuum-distilled from KOH. Silica gel (Wakogel C-200) was used for column chromatography. The 8.97% O_2 in N_2 mixture and the 995 ppm of CO in N_2 mixture were commercially obtained.

Synthesis. 5β,15β-Bis(2-pentanamidophenyl)-10α,20α-bis(nonanediamidodi-*o*-phenylene)porphyrin (H_2-Az-val$\beta\beta$), 5β,15β-Bis[2-(2,2-dimethylpropanamido)phenyl]-10α,20α-bis(nonanediamidodi-*o*-phenylene)porphyrin (H_2-Az-piv$\beta\beta$), 5,15-diphenyl-10α,20α-bis(nonanediamidodi-*o*-phenylene)porphyrin (H_2-Az-P), and their cobalt(II) complexes were prepared by the previously described method.[1]

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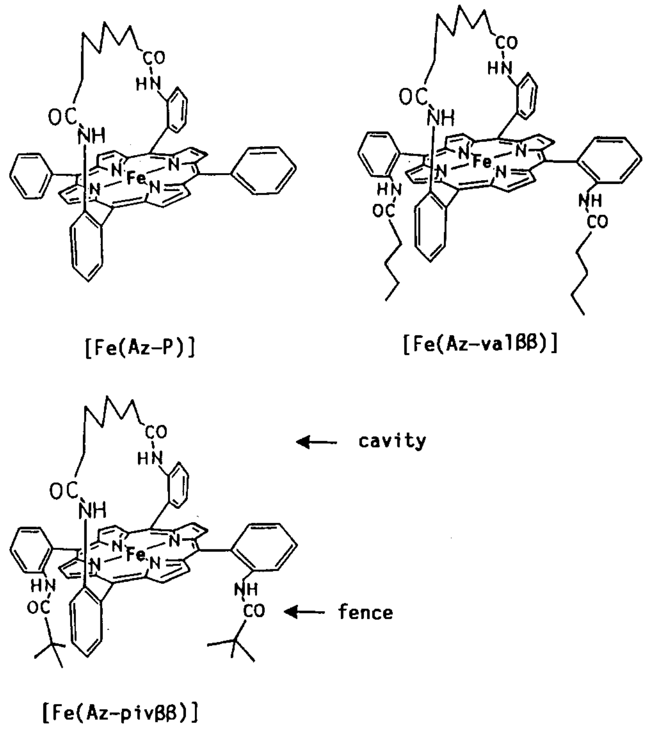
Table I. ^{1}H NMR Data for O_2 and CO Adducts of "Jellyfish" Type Iron(II) Porphyrins[a]

	methylene[b]					
	δ	γ	β	α	amide[c]	2-Me[d]
[Fe(Az-P)(1,2-Me_2Im)(CO)]	−1.02	+0.11	+0.57	+0.57	5.83	−1.93
[Fe(Az-P)(1,2-Me_2Im)(O_2)]	−0.98	+0.17	+0.95	+1.28	7.96, 4.56	−1.45
[Fe(Az-val$\beta\beta$)(1,2-Me_2Im)(CO)]	−1.05	+0.10	+0.55	+0.55	5.69	−1.82
[Fe(Az-val$\beta\beta$)(1,2-Me_2Im)(O_2)]	−1.01	+0.15	+0.93	+1.26	7.88, 7.77 5.35, 4.76	−1.43 −1.17
[Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)(CO)]	−1.02	+0.07	+0.16	+0.76	5.67	−1.83
[Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)(O_2)]	−1.25	+0.09	+0.57	+1.33	7.73, 4.65	−1.40

[a] Chemical shifts (ppm) from TMS in toluene-d_8; measured at −20 and 24 °C for the O_2 adducts and CO adducts, respectively. [b] Protons in strapped heptamethylene:

$$-COCH_2CH_2CH_2CH_2CH_2CH_2CH_2CO-$$
$$\alpha \quad \beta \quad \gamma \quad \delta \quad \gamma \quad \beta \quad \alpha$$

[c] Amide protons in strapped chain. [d] Protons in the 2-methyl group of 1,2-Me_2Im.



[Fe(Az-P)]

[Fe(Az-val$\beta\beta$)]

[Fe(Az-piv$\beta\beta$)]

Figure 1. "Jellyfish" type iron(II) porphyrins.

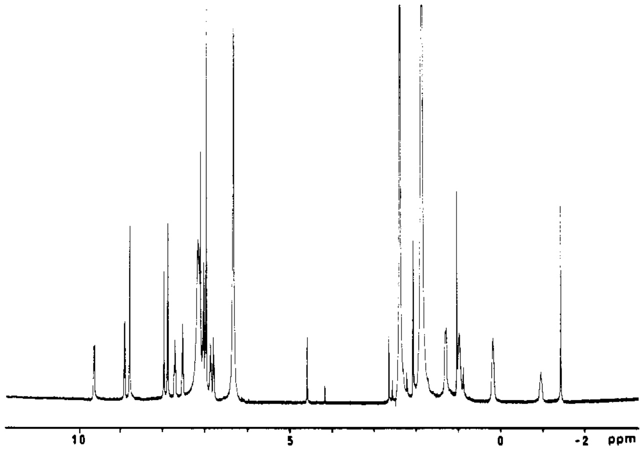


Figure 2. ^{1}H NMR spectrum of the O_2 adducts of [Fe(Az-P)] ca. 5 × 10^{-3} M in toluene-d_8 containing 1,2-Me_2Im (0.07 M) at −20 °C.

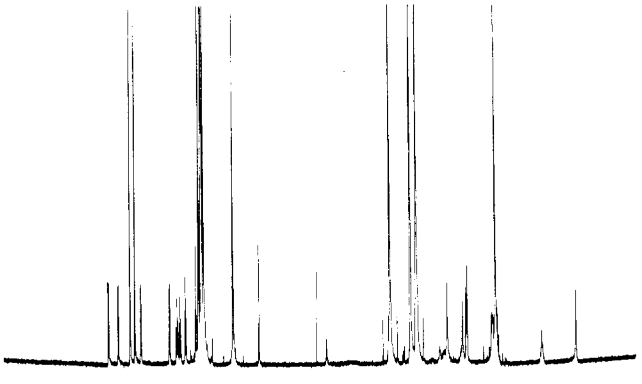


Figure 3. ^{1}H NMR spectrum of the CO adducts of [Fe(Az-piv$\beta\beta$)] ca. 5 × 10^{-3} M in toluene-d_8 containing 1,2-Me_2Im (0.07 M) at 24 °C.

Fe(III) Insertion. Iron(III) complexes were prepared by heating the porphyrins with $FeBr_2$ in acetic acid containing 2% sodium acetate (w/w) at 50 °C. Purification was accomplished with a silica gel column using $CHCl_3/CH_3OH$ (99:1) as an eluent. The product was evaporated to dryness and then treated with concentrated HBr in $CHCl_3$. After being dried over Na_2SO_4, the solvent was reduced in volume on a rotary evaporator, and the products were precipitated by adding hexane.

[Fe(Az-P)]Br. Anal. Calcd for $C_{53}H_{42}N_6O_2FeBr$: C, 68.40; H, 4.55; N, 9.03. Found: C, 68.31; H, 4.40; N, 8.76. UV-vis λ_{max} ($CHCl_3$): 420 nm (log ϵ 4.91), 515 (4.12), 584 (3.46), 668 (3.41), 695 (3.49).

Fe(Az-val$\beta\beta$)]Br. Anal. Calcd for $C_{63}H_{60}N_8O_4FeBr$: C, 67.02; H, 5.36; N, 9.93. Found: C, 66.11; H, 4.82; N, 10.15. UV-vis λ_{max} ($CHCl_3$): 419 nm (log ϵ 4.95), 513 (4.13), 584 (3.57), 656 (3.49), 684 (3.48).

Fe(Az-piv$\beta\beta$)]Br. Anal. Calcd for $C_{63}H_{60}N_8O_4FeBr{\cdot}0.5CHCl_3$: C, 64.16; H, 5.13; N, 9.43. Found: C, 63.50; H, 4.96; N, 9.29. UV-vis λ_{max} ($CHCl_3$): 421 nm (log ϵ 4.93), 512 (4.14), 583 (3.54), 658 (3.49), 684 (3.49).

Results and Discussion

The Fe(III) complexes were prepared by heating the porphyrins with $FeBr_2$ in acetic acid containing sodium acetate. The reaction temperatures were kept below 50 °C to prevent isomerization of pivalamide and valeramide groups. The lack of isomerization was confirmed by ^{1}H NMR spectra of the O_2 and CO adducts (Figures 2 and 3; Table I). The methylene proton resonances in the cavities appeared as four multiplets in both [Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)(CO)] and [Fe(Az-val$\beta\beta$)(1,2-Me_2Im)(O_2)]. Since these resonances appeared as six multiplets in isomers such as H_2-Az-piv$\alpha\beta$ and H_2-Az-val$\alpha\beta$,[1] any isomerization of pivalamide groups and valeramide groups was not detectable.

Table II lists the data for eq 1–3. Here, P represents porphyrins, K_{O_2} and K_{CO} are equilibrium constants and are equal to $1/P_{1/2}(O_2)$

$$[Co(P)(1,2\text{-}Me_2Im)] + O_2 \xrightleftharpoons{K_{O_2}} [Co(P)(1,2\text{-}Me_2Im)(O_2)] \quad (1)$$

$$[Fe(P)(1,2\text{-}Me_2Im)] + O_2 \xrightleftharpoons{K_{O_2}} [Fe(P)(1,2\text{-}Me_2Im)(O_2)] \quad (2)$$

$$[Fe(P)(1,2\text{-}Me_2Im)] + CO \xrightleftharpoons{K_{CO}} [Fe(P)(1,2\text{-}Me_2Im)(CO)] \quad (3)$$

and $1/P_{1/2}(CO)$, respectively. The axial base employed for the measurements of both O_2 and CO affinities was 1,2-dimethyl-

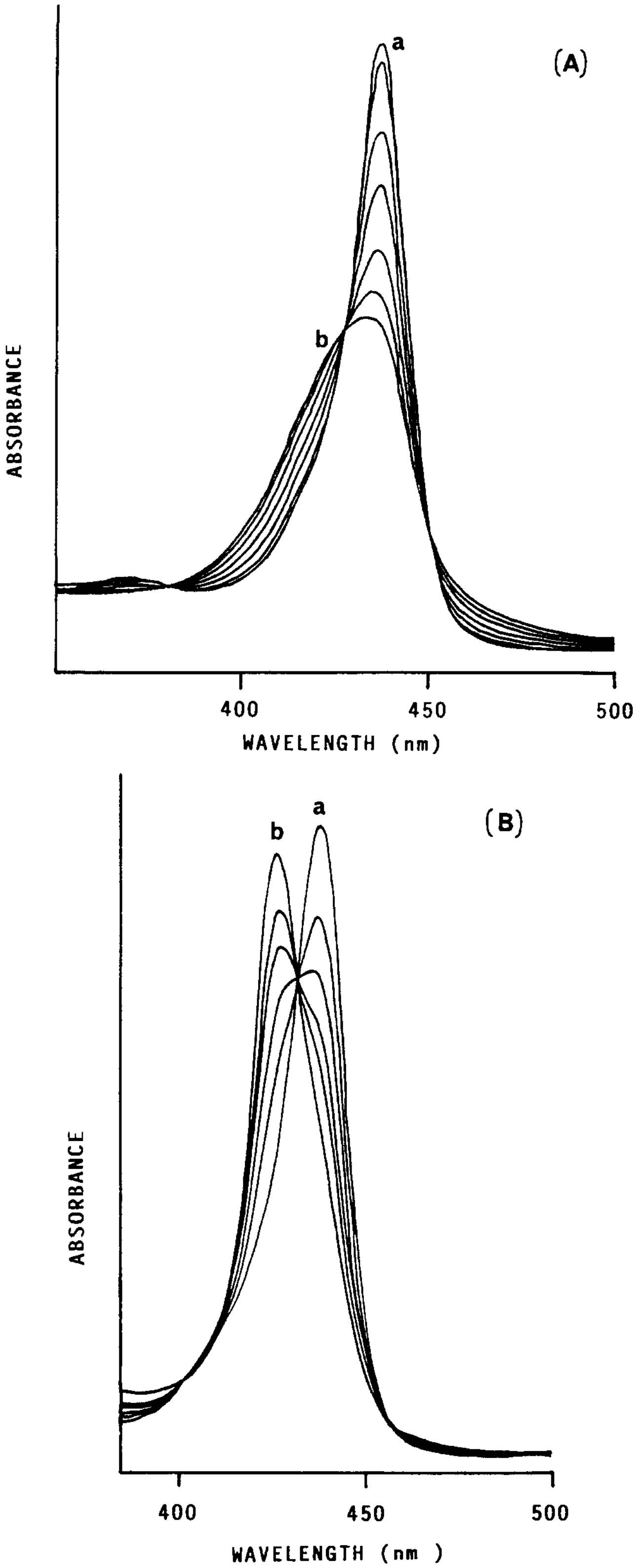


Figure 4. (A) Spectral changes upon addition of O_2 to [Fe(Az-piv$\beta\beta$)] ca. 1 × 10^{-5} M in toluene (0.07 M 1,2-Me_2Im, 25 °C): (curve a) under N_2; (curbe b) under 760 Torr of O_2. The following partial pressures of O_2 were used: 14.9, 75.9, 152, 304, and 506 Torr. (B) Spectral changes upon addition of CO to [Fe(Az-piv$\beta\beta$)] ca. 1 × 10^{-5} M in toluene (0.07 M 1,2-Me_2Im, 25 °C): (curve a) under N_2; (curve b) under 0.746 Torr of CO. The following partial pressures of CO were used: 0.076, 0.157, 0.260, and 0.386 Torr.

Table II. O_2 and CO Binding to Model Complexes[a]

	$P_{1/2}(O_2)$, Torr	$P_{1/2}$(CO), Torr
[Fe(Az-P)(1,2-Me_2Im)]	27	0.083
[Fe(Az-val$\beta\beta$)(1,2-Me_2Im)]	12	0.029
[Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)]	269	0.27
[Fe(TpivPP)(1,2-Me_2Im)][b]	38	0.0089
[Co(Az-P)(1,2-Me_2Im)]	378	
[Co(Az-val$\beta\beta$)(1,2-Me_2Im)]	1013	
[Co(Az-piv$\beta\beta$)(1,2-Me_2Im)]	13000[c]	
[Co(TpivPP)(1,2-Me_2Im)][d]	900	

[a] In toluene containing 0.07 M 1,2-Me_2Im at 25 °C; estimated errors <15%. [b] Reference 7. [c] Extraporated from the van't Hoff plots; estimated error <30%. [d] Reference 3.

imidazole (1,2-Me_2Im), which is known to preferentially form monoligated complexes.[7,8] The O_2 and CO bindings were found to be reversible, as stated in the Experimental Section. As shown in Figure 4, well-defined isosbestic points were observed in O_2 and CO titrations of jellyfish Fe(II) porphyrins. Thus, the presence of bisligated complexes can be considered negligible.[9]

It has been confirmed that the bindings of 1,2-Me_2Im to jellyfish Co(II) porphyrins occur on the fence sides, as the strapped heptamethylene chain inhibits the binding of axial bases on the cavity sides.[1] The binding of 1,2-Me_2Im to [Fe(Az-P)] occurs on the fence side as well, as reversible O_2 binding was observed; if 1,2-Me_2Im binds on the cavity side of [Fe(Az-P)], the O_2 binding side of [Fe(Az-P)] is identical with that of [Fe(TPP)].[10] [Fe(TPP)] did not bind O_2 reversibly at room temperature under our experimental conditions.[11] As the fences in both [Co(Az-val$\beta\beta$)] and [Co(Az-piv$\beta\beta$)] enforce the axial base binding on the fence side,[1] the binding site of their Fe(II) analogues is expected to be only the fence side. Additionally, ^{1}H NMR data for [Fe(Az-val$\beta\beta$)(1,2-Me_2Im)(CO)] and [Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)(CO)] did not show any evidence suggesting the binding of 1,2-Me_2Im on the cavity side (see below). Thus, it is concluded that the bindings of 1,2-Me_2Im to jellyfish porphyrinato Co(II) and Fe(II) complexes take place on the fence sides, while both O_2 and CO bind to the cavity sides.

The O_2 and CO affinities of Fe(II) porphyrins decrease in the order [Fe(Az-val$\beta\beta$)(1,2-Me_2Im)] > [Fe(Az-P)(1,2-Me_2Im)] > [Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)]. This is not the same order as expected from our earlier prediction[1] based on the changes in the strength of the π–π interaction between metal and axial base: [Fe(Az-P)(1,2-Me_2Im)] > [Fe(Az-val$\beta\beta$)(1,2-Me_2Im)] > [Fe(Az-piv$\beta\beta$)(1,2-Me_2Im)]. Our prediction was that the O_2 affinities would be reduced when the axial base orientation (ϕ) was equal to 45° by the steric repulsion with the fences. This would be a result of the overlap between the π oribtal (dπ or pπ) of Co and the pπ orbital of N on the axial base reaching a minimum at ϕ = 45°.[12] To check the effects on axial bases, the O_2 affinities of corresponding Co(II) porphyrins were measured by using 1,2-Me_2Im as an axial base. As shown in Table II, the O_2 affinities of Co(II) porphyrins reduce in the order [Co(Az-P)(1,2-Me_2Im)] > [Co(Az-val$\beta\beta$)(1,2-Me_2Im)] > [Co(Az-piv$\beta\beta$)(1,2-Me_2Im)]. This is the same order observed for the O_2 affinities of Co(II) porphyrins by using pyridine or 1-MeIm as an axial base.[1] From these results, the difference between the O_2 affinities of Fe(II) and Co(II) porphyrins was detectable.

What factor should be responsible for the changes in the order of O_2 affinities for the Fe(II) complexes of jellyfish porphyrins compared with those of Co(II) complexes? ^{1}H NMR spectra were measured for the O_2 and CO adducts of the Fe(II) porphyrins to examine the conformation of cavities. As seen in Table I, the signals of amide protons and methylene protons in the cavities appeared at similar positions for both [Fe(Az-P)(1,2-Me_2Im)-

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(10) Abbreviations used: TPP, dianion of *meso*-tetraphenylporphyrin; TpivPP, dianion of *meso*-5α,10α,15α,20α-tetrakis(*o*-pivalamidophenyl)porphyrin; HIm, imidazole; $V/\lambda = g_1/(g_3 + g_2) + g_2/(g_3 - g_1)$; $\Delta/\lambda = g_1/(g_3 + g_2) + g_3/(g_2 - g_1) - V/2\lambda$.

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Table III. EPR Parameters for Bis Axial Base Adducts of Iron(III) Porphyrins

	g_1	g_2	g_3	V/λ	Δ/λ	V/Δ	remarks
[Fe(Az-P)(1-MeIm)$_2$]$^+$	1.65	2.27	2.89	2.30	3.57	0.64	species I
	1.52	2.29	2.89	1.95	3.08	0.63	species II
[Fe(Az-valββ)(1-MeIm)$_2$]$^+$	1.54	2.29	2.89	1.99	3.15	0.63	species I
	1.44	2.24	3.01	1.70	3.19	0.53	species II
[Fe(Az-pivββ)(1-MeIm)$_2$]$^+$	1.64	2.28	2.83	2.24	3.62	0.62	species I
	1.51	2.28	2.92	1.91	3.13	0.61	species II
[Fe(TPP)(1-MeIm)$_2$]$^{+a}$	1.55	2.29	2.88	2.02	3.18	0.64	
[Fe(TPP)(ImH)$_2$]$^{+b}$	1.59	2.32	2.84	2.16	3.12	0.69	$\phi = 6°$
	1.47	2.2	3.00	1.72	3.53	0.49	$\phi = 41°$

[a] Reference 21. [b] Reference 2.

(CO)] and [Fe(Az-valββ)(1,2-Me$_2$Im)(CO)]. Contrary to this, the methylene proton signals of the strapped chain in [Fe(Az-pivββ)(1,2-Me$_2$Im)(CO)] appeared at positions different from those of the other two CO adducts. These results imply that the CO molecule in [Fe(Az-pivββ)(1,2-Me$_2$Im)(CO)] experiences different interactions with the methylene protons in the cavity compared to the other two CO adducts. Such steric interactions[5,9,13] must be responsible for the reduced CO affinity of [Fe(Az-pivββ)(1,2-Me$_2$Im)]. The changes in CO affinities between [Fe(Az-P)(1,2-Me$_2$Im)] and [Fe(Az-valββ)(1,2-Me$_2$Im)], however, cannot be explained by steric or polar effects in the cavities, since the differences in the conformation of cavities were not observed in the ^{1}H NMR spectra.

In the case of the O$_2$ adducts, the amide groups in the cavities are known to play a major role in the determination of O$_2$ affinities.[14-16] The signals of amide groups in the cavity of [Fe(Az-P)(1,2-Me$_2$Im)(O$_2$)] appeared at 7.96 and 4.56 ppm. As pointed out by Momenteau et al.,[16] the splitting of the amide protons is due to the H-bonding with O$_2$. In [Fe(Az-pivββ)(1,2-Me$_2$Im)(O$_2$)], the amide protons appeared at similar positions, while the methylene proton signals in the cavity differed from those of the other two complexes. Thus, it may be concluded that the cavity's steric effect is responsible for the reduced O$_2$ affinity of [Fe(Az-pivββ)(1,2-Me$_2$Im)]. In the case of [Fe(Az-valββ)(1,2-Me$_2$Im)(O$_2$)], the presence of two sets of amide proton signals may be responsible for the higher O$_2$ affinity as compared to that of [Fe(Az-P)(1,2-Me$_2$Im)]. In addition, it is interesting to note that the cavity conformation was varied with the fence appended to the meso phenyl in the porphyrin and that the porphyrin rings were found to be flexible. Furthermore, the split resonances of 2-Me protons in 1,2-Me$_2$Im may imply the existence of two species having different axial base orientations; the correlation between the chemical shifts of the 2-Me protons and the axial base orientation cannot be deduced, however, because the 2-Me proton signals of [Fe(Az-pivββ)(1,2-Me$_2$Im)(O$_2$)] appear at −1.40 ppm as an singlet.

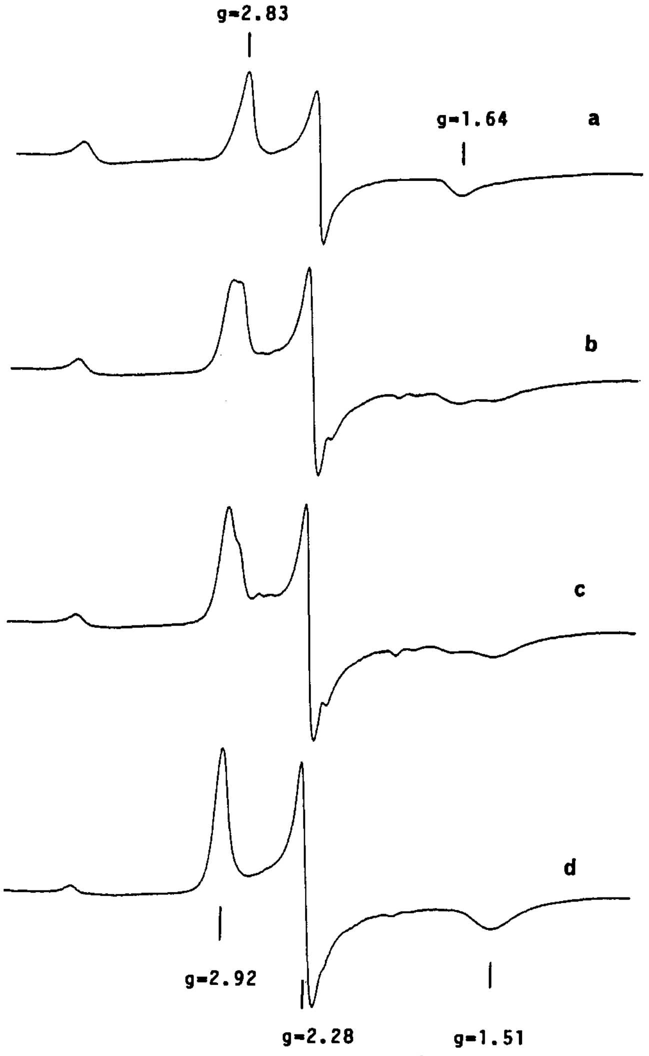

Figure 5. EPR spectra at 77 K of ca. 5 × 10^{-5} M [Fe(Az-pivββ)]Br in CDCl$_3$ in the presence of various concentrations of 1-MeIm: (a) ca. 1 × 10^{-4} M; (b) 5 × 10^{-4} M; (c) 1 × 10^{-3} M; (d) 1.1 × 10^{-2} M.

An attempt has been done to examine the orientation of axial bases in jellyfish Fe(II) porphyrins. By the steric repulsion between the porphyrin plane and the axial base,[17] the length of the Fe–N (1,2-Me$_2$Im) bond has been known to elongate with decreasing ϕ. The difference in length is ca. 0.07 Å upon changes in ϕ from 7 to 23°.[18,19] Recently, from the study on single-crystal EPR spectra of low-spin Fe(III) porphyrins, Quinn et al.[2] have shown that the crystal field parameter (V/Δ) decreases with increasing orientation of the axial bases (ϕ). Thus, the EPR spectra of jellyfish Fe(III) porphyrins were measured to examine whether fences of the Fe(III) porphyrins can control the orientation of axial bases. As shown in Figure 5, a set of signals (g = 2.83, 2.28, 1.64) appears upon addition of 1-MeIm (ca. 1 equiv) to [Fe(Az-pivββ)]Br in CDCl$_3$ at 77 K, further addition of 1-MeIm gives another set of signals (g = 2.92, 2.28, 1.51), and only the latter set of signals is observed upon addition of a 100-fold excess of 1-MeIm. Similar spectral changes were obsered for both [Fe-(Az-P)]Br and [Fe(Az-valββ)]Br. The g values for these signals are characteristics of low-spin 1-MeIm bisadducts of Fe(III) porphyrins.[20-24] In the absence of 1-MeIm, the Fe(III) porphyrins

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have EPR spectra that are typical of high-spin Fe(III) porphyrins (g = ca. 6). Thus, it is demonstrated that the amide groups do not bind to the iron center. Furthermore, Walker et al.[22] have also observed two sets of EPR signals in the crystal of [Fe(TPP)(ImH)$_2$]Cl. It has been shown from an X-ray crystallographic study[25] that two sets of EPR signals are due to the existence of two distinct species having different orientations (ϕ) of axial bases. Therefore, it is speculated that the two sets of EPR signals observed in this work are due to the existence of the two species having different ϕ's. The crystal field parameters were calculated by the method of Taylor[26] and are summarized in Table III. The V/Δ values of species II were smaller than those of the corresponding species I, where both species I and II refer to those existing at low and high axial base concentrations, respectively. In species I the V/Δ values do not change as much as those found by Quinn et al.;[2] however, the V/Δ values decrease in the order [Fe(Az-P)(1-MeIm)$_2$]$^+$ > [Fe(Az-val$\beta\beta$)(1-MeIm)$_2$]$^+$ > [Fe(Az-piv$\beta\beta$)(1-MeIm)$_2$]$^+$. In species II, the V/Δ values decrease in the order [Fe(Az-P)(1-MeIm)$_2$]$^+$ > [Fe(Az-piv$\beta\beta$)(1-MeIm)$_2$]$^+$ > [Fe(Az-val$\beta\beta$)(1-MeIm)$_2$]$^+$. The changes in V/Δ, and thus ϕ, do not show the same trends in both species I and II. Therefore, our attempt to demonstrate that the axial base orientation is controlled by the steric restriction was unsuccessful.

The results obtained from this study are summarized as follows: (1) The reduction of O_2 affinities of jellyfish Fe(II) porphyrins is not in the same order as for the O_2 affinities of the corresponding Co(II) porphyrins. These changes in O_2 and CO affinities in the Fe(II) porphyrins cannot be explained only by the axial base orientation. (2) From the ^{1}H NMR study, the conformations of cavities in both O_2 and CO adducts of [Fe(Az-piv$\beta\beta$)(1,2-Me$_2$Im)] were found to differ from each other. These conformational changes in the cavities are responsible for the reduced O_2 and CO affinities for [Fe(Az-piv$\beta\beta$)(1,2-Me$_2$Im)] as compared with those for [Fe(Az-P)(1,2-Me$_2$Im)]. Nevertheless, it is evident that the O_2 and CO affinities for the Fe(II) porphyrins are not fully explained by the conformational changes in the cavities, since the ^{1}H NMR spectra of the cavities in [Fe(Az-P)(1,2-Me$_2$Im)(CO)] and [Fe(Az-val$\beta\beta$)(1,2-Me$_2$Im)(CO)] were virtually identical. Only the irregularity in these CO affinities remains as a question, and we propose further research to clarify these results.

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Thiolato–Technetium Complexes. 3.[1] Synthesis and X-ray Structural Studies on the Geometrical Isomers *cis*- and *trans*-Bis(*p*-chlorobenzenethiolato)bis(1,2-bis(dimethylphosphino)ethane)technetium(II)

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The reaction of *trans*-[Tc^{V}(OH)(O)(DMPE)$_2$]$^{2+}$ with excess *p*-chlorobenzenethiol and a small amount of base produces both cis and trans isomers of the air-stable arenethiolato–Tc(II) complex [Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$]. The geometries of these complexes are confirmed by X-ray crystallography. *cis*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$], chemical formula $TcCl_2S_2P_4C_{24}H_{40}$, crystallizes in the orthorhombic space group *Iba*2 with $Z = 4$ and lattice parameters a = 10.4840 (14) Å, b = 16.505 (2) Å, and c = 17.783 (4) Å. The final weighted R value is 0.024. The coordination sphere is octahedral with Tc occupying a crystallographic 2-fold axis. Important molecular parameters are Tc–S = 2.424 (3) Å, Tc–P(trans to P) = 2.385 (2) Å, Tc–P(trans to S) = 2.439 (3) Å, and Tc–S–C = 114.0 (3)°. Thus, there is a significant (0.054 (4) Å) sulfur-induced structural trans effect. *trans*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$], chemical formula $TcCl_2S_2P_4C_{24}H_{40}$, crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$ and lattice parameters a = 9.882 (2) Å, b = 15.311 (3) Å, c = 10.285 (2) Å, and β = 96.226 (12)°. The final weighted R value is 0.032. The coordination sphere is octahedral with Tc occupying a crystallographic inversion center. Important molecular parameters are Tc–S = 2.424 (2) Å, Tc–P = 2.397 (2) Å, and Tc–S–C = 123.8 (2)°. The cis isomer is considerably more stable than the trans; trans → cis isomerization occurs with a half-life of about 74 min in dichloromethane at room temperature. The cis isomer exhibits a reversible Tc(III/II) redox couple at −0.182 V vs Ag/AgCl and a nonreversible Tc(II/I) couple at about −0.99 V vs Ag/AgCl. The remarkable stability of *cis*-[Tc(SC$_6$H$_4$-*p*-Cl)$_2$(DMPE)$_2$] in the Tc(II) oxidation state and in the cis geometry is discussed in terms of the electronic and steric properties of the aryl substituent.

Introduction

While thiolato–technetium complexes containing technetium in the +5 or +6 oxidation states are well-known,[5] such complexes containing low-valent technetium centers are relatively rare.[6,7] We have recently introduced[1] a general preparative route to the thiolato–Tc(III) comlexes *trans*-[Tc(SR)$_2$(DMPE)$_2$]$^+$, where $^-$SR is an alkane- or benzenemethanethiolato ligand and DMPE is 1,2-bis(dimethylphosphino)ethane. These complexes exhibit reversible Tc(III/II) redox couples, although the resulting Tc(II) species are not sufficiently stable to be isolated. In the hopes of generating more stable Tc(II) complexes, we have extended our preparative route to include arenethiolato ligands. In this paper we report the somewhat unexpected results of this investigation, including the isolation and characterization of both trans and cis

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