Å, respectively, and the polymetallates Sb_4^{2-} and Sb_7^{3-}. The distances in Sb_4^{2-} are rather short (average 2.75 Å, bond order = 1.25 from MO theory) and very close to the value obtained in **5**.[34] In Sb_7^{3-} the distances vary between 2.717 (2) and 2.906 (2) Å.[34] Interestingly the Sb–Sb distance, 2.663 Å, in [*trans*-η^2-$\{(CO)_5WSb(Ph)Sb(Ph)W(CO)_5\}W(CO)_5$], which is thought to have a bond order of about 1.5, is also very close to the values seen in **5**.[35] The above data suggest that the Sb–Sb "single" bond in **5** is significantly shorter than expected. Shortened E–E distances have been seen in species such as $[P\{P(O)(O\text{-}i\text{-}Pr)_2\}_2]^-$ [36] and $[P\{P(O)Ph_2\}_2]^-$ [37] (P–P = 2.12–2.15 Å) where p–d π bonding has been cited as a factor in shortening the P–P bonds. It may be possible that a similar interaction is occurring here. The SbSbSb angle of 88.8 (1)° is acute. This is difficult to account for in terms of Bent's rule unless the $SbPh_2$ group is considered to be a more electronegative substituent than Ph, which seems unlikely. The Sb(2)Sb(2)′ distance is 3.864 (1) Å, ruling out significant bonding interactions between these atoms.

One other structural feature detailed in Table II concerns the dihedral angles between the phenyl rings. It is apparent that there is a rough correlation between this parameter and the C–E–C angle, but no correlation that would indicate a multiple bonding interaction between the π levels in the phenyl rings and the main group 5 central atom.

In conclusion, the results in this paper show that (i) 12-crown-4 is a useful reagent in abstracting lithium ions from their $[ER_2]^-$ (E = P, As, or Sb) salts, forming rare two-coordinate group 5 anions; (ii) the structures of the arsenic complexes are significantly different from their phosphorus and antimony analogues; (iii) it is probable that lithium derivatives of terminal amides are mostly planar, whereas the monomeric heavier element derivatives are pyramidal at the pnictide; (iv) it may also be possible to solubilize main group 5 elements such as As, Sb, or Bi in solutions of their $LiER_2$ derivatives in the same way that phosphorus has been solubilized with soft anionic bases.[37]

Acknowledgment. We thank the NSF and the Committee on Research of the University of California for financial support.

Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond distances and angles, and hydrogen coordinates (28 pages). Ordering information is given on any current masthead page.

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Artificial Allosteric System. 4. T/R Characterization of an Artificial Allosteric System by Resonance Raman Spectroscopy and O_2 or CO Affinity

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Abstract: Selective preparation of a pentacoordinate gable porphyrin·Fe^{II}_2·α,ω-diimidazolylpropane which serves as a model for R-state Hb was achieved (ca. 97%). Its CO affinity and resonance Raman spectrum were studied in order to compare it with the corresponding pentacoordinate T complex previously prepared by use of diimidazolylmethane as a bridging ligand. Imidazolylpropionylamido-TPP·Fe^{II} was newly prepared as a T model to compare its CO affinity and resonance Raman spectrum with the corresponding R model, imidazolylvaleramido-TPP·Fe^{II}. These T/R couples combined with known T/R couples—Hb $\alpha_2\beta_2$ vs. isolated α or β; Fe^{II}·TpivPP·DMI (1,2-dimethylimidazole) vs. Fe^{II}·TpivPP·1MI (1-methylimidazole); Fe^{II}·pocket porphyrin·DMI vs. Fe^{II}·pocket porphyrin·1MI—confirm that structural differentiation of the T state from the R state is conveniently made by considerable low-frequency shift by 8–34 cm^{-1} in the resonance Raman ν_{Fe-N} stretch and remarkable decrease in CO and O_2 affinities. The observed CO and O_2 affinity changes due to T → R structure change are ranging between 33 and 420 for $K_{O_2}(R)/K_{O_2}(T)$ and between 40 and 750 for $K_{CO}(R)/K_{CO}(T)$. On the basis of these appropriate T- and R-structure models, the magnitudes of cooperativity operating in O_2 and CO binding to native (Hb, number of cooperative sites $n = 4$) and artificial (gable·Fe^{II}, $n = 2$) allosteric systems, defined by $(K_n/K_1)/(K_R/K_T)$, were estimated to be considerably smaller than unity, suggesting that the R forms of the allosteric systems are not fully relaxed compared to the "ideal" R form independently prepared.

Allosteric control of successive O_2 binding to hemoglobin (Hb) is best interpreted by remarkable conformation change from the low O_2 affinity form, T (tense), to the high O_2 affinity form, R (relaxed), on O_2 binding to the subunit protein (α or β) in the tetrameric protein ($\alpha_2\beta_2$).[1] The conformation change in the *oxy* subunit(s) further causes induced T → R conformation change in the *deoxy* subunit.

The allosteric effect itself is well characterized by the sigmoid curve in isothermal O_2 binding (cooperativity) on one hand, while T and R structures are characterized by X-ray[2] or EXAFS[2] only in limited examples. However, selective preparation of artificial

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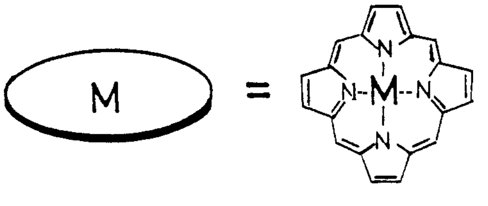
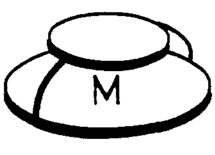
Table I. Base Association Constants and Optimal Formation of Pentacoordinate Porphyrin·Fe^{II}·B Complexes[a]

type	porphyrin	ligand	log K_5	log K_6	K_5/K_6	penta, %
i	TPP	DMI[c]	4.43	0.39	11 000	98[f]
	TPP	HIm[b]	3.9	4.9	0.1	14[b]
	TPP	CO[c]	4.82	2.14	470	92[h]
ii	capped	1MI[c]	3.31	0.77	350	90[i]
	TpivPP	1MI[e]	4.8	3.5	20	94[j]
	MedPoc	1MI[d]	4.46	−0.7	140 000	>99[k]
iii	tailed	*e*	2.4[l]	2.0[l]	2.3[l]	>90[l]
iv	Fe^{II}_2·gable	DIM[e]	7.7	4.9	~630	96[m]
	Fe^{II}_2·gable	DIP[e]	7.8	4.5	2 000	97[m]

[a] Abbrevations used are as follows: TPP, *meso*-tetraphenylporphyrinato; capped 5,10,15,20-[pyromellitoyltetrakis(o-oxyethoxyphenyl)]-porphyrinato; MedPoc, 5,10,15-[(1,3,5-benzenetriyltripropionyl)tris(α,α,α-*o*-aminophenyl)]-20-(α-*o*-pivalamidophenyl)porphyrinato; tailed, dianion of deuteroporphyrin 6-methyl ester 7-histidine methyl ester; HbA, native hemoglobin, adult; Mb, native myoglobin; TpivPP, *meso*-tetrakis(α,α,α,α-*o*-pivalamidophenyl)porphyrinato; DMI, 1,2-dimethylimidazole; 2MI, 2-methylimidazole; 1MI, 1-methylimidazole; PocPiv, 5,10,15-[(1,3,5-benzenetriyltriacetyl)tris(α,α,α-*o*-aminophenyl)]-20-(α-*o*-pivalamidophenyl)porphyrinato; TPP-3CIm, *meso*-5-[*o*-(3-(*N*-imidazolyl)propionamido)-phenyl]-10,15,20-triphenylporphyrinato; TPP-5CIm, *meso*-5-[*o*-(5-(*N*-imidazolyl)valeramido)phenyl]-10,15,20-triphenylporphyrinato; gable, 3; DIM, di-*N*-imidazolylmethane; DIE, 1,2-di-*N*-imidazolylethane; DIP, 1,3-di-*N*-imidazolylpropane. [b] imidazole, $[HIm]_{free} = 1 \times 10^{-4}$ M, in benzene. [c] In toluene, 23 °C. [d] In toluene, 25 °C. [e] In benzene, 25 °C. [f] Reference 3g. [g] Reference 6. [h] Reference 6b. [i] Reference 3c. [j] Reference 3n. [k] Reference 3p. [l] *Reference* 4d, e, g; $K_5 = 230$, $K_6 = 10^2$ M^{-1}. [m] This work, $[Fe^{II}_2\text{·gable}] = 5 \times 10^{-6}$ M.

*penta*coordinate T and R complexes has not yet been successful, except in such elaborate approach as capped or face-to-face porphyrin (**1**)[3] and tailed porphyrin (**2**).[4] Even for these sophisticated examples, preparation of a porphyrin capable of assuming interconvertible T and R forms of the same (or very similar) local structure is not possible except our previous molecular systems,[5] in which the R form seems to be produced as an intermediate but without firm spectroscopic evidence.





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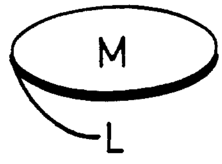
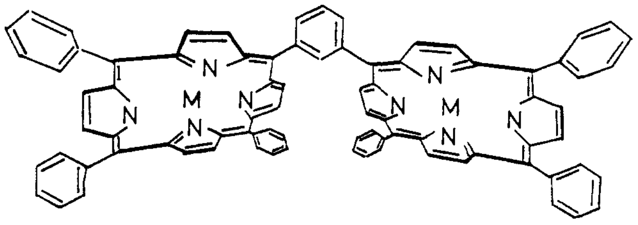
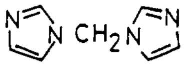


2

In this article, we report selective preparation of stable T and R pentacoordinate gable porphyrin complexes (**3**)·Fe^{II}_2·B by the use of bridging bifunctional ligands (**4**) of appropriate linking units[5]



3a: M = Fe^{II}
3b: M = Zn^{II}

4a:


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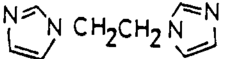

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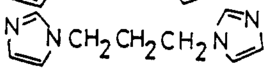

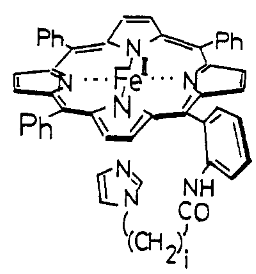

5: *i* = 2 and 4

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as B, where the T ⇄ R structural change is simply controlled by change in the arm length, *m*, without any undesirable structure perturbation. the R complex thus formed seems to serve as an "ideal" model for the R form in the artificial allosteric system.

We also would like to report here resonance Raman (RR) spectra of **3**·Fe^{II}_2·**4** complexes and related monomeric T and R complexes. Raman spectroscopy is shown to serve as appropriate tool for characterization of the T and R structures.

Results and Discussion

A pentacoordinate porphyrin·Fe^{II}·base complex is formed as a transient species when a tetracoordinate complex of an ordinary iron porphyrin like TPP·Fe^{II} is titrated with an ordinary base like imidazole.[6] It is mainly due to the ready hexacoordination taking place after pentacoordination, where K_5/K_6 ranges from 0.1 to 1 as exemplified in Table I. At the moment, three approaches are available for selective preparation of stable pentacoordinate complexes: (i) using a bulky base such as 1,2-dimethylimidazole to retard the base approach to the porphyrin·Fe^{II} plane[7] from both sides, (ii) preparing a "face-to-face" or "capped" porphyrin·Fe^{II} complex, which has too small of a space to accommodate a sixth base,[3] and (iii) using a "tailed" porphyrin·Fe^{II} complex, which has a tail base linked covalently through an adjustable arm.[4]

Among these three, the first approach may suffer the limitation that the pentacoordinate T/R couple is available only with considerable difference in base structure (e.g., 1-methylimidazole vs. 1,2-dimethylimidazole), making direct T/R comparison difficult. A limitation of the other approaches may come either from the porphyrin plane bending on too short capping (in the case of capped porphyrins) or from considerable entropy loss in pentacoordination with a tail base connected by a long arm (tailed porphyrins).

We have been investigating metallogable porphyrins as promising artificial allosteric systems.[5] As we have reported previously, **3**·M_2 complexes bind dimeric ligand **4a** from the endo,endo side,[5d] forming stable, bridged pentacoordinate complexes. For **3**·Zn^{II} and **4a**, the observed K_{endo}/K_{exo} amounted to more than 10^2, favoring strongly endo coordination entropically. As a result, pentacoordination is greatly favored to give $K_5/K_6 = 630$, due to the favored endo coordination. A great advantage in the gable system is to provide interconvertible T ⇄ R states of the same (or very similar) local structures. However, a corresponding stable R-complex model has not been available.

Selective Preparation of Pentacoordinate T and R Porphyrin·Fe^{II}·B Complexes for Allosteric and Nonallosteric Systems. Bridging dimeric imidazoles with different linking arm lengths, **4b**, and **4c**, were newly prepared for the preparation of the stable pentacoordinate R complexes, and complex formation between **4a–c** and **3**·M_2 was studied spectroscopically by using electronic, NMR, and resonance Raman spectroscopies (RR). In situ formation (up to 97%) of the corresponding pentacoordinate complex in a benzene solution was observed when an appropriate amount of a base was employed. The results sharply contrast the TPP·Fe^{II}/imidazole couple, where less than 14% of the pentacoordinate complex is formed, at most, based on the observed titration profile. The results are summarized in Table I. Again, remarkably favored endo,endo coordination over exo is mainly responsible for the observed unusual enhancement in the K_5/K_6 ratio, 1300–350 for the gable·Fe^{II}/bridging base systems vs. 1–0.11 for TPP·Fe^{II}/monomeric base systems.

On the basis of the CPK molecular model, some excess strain in the molecular framework or in the coordination bond together with out-of-plane movement of the central metal ion is expected for the shortest briding base **4a**, while none or very small excess strain is expected for longer bridging bases **4b** and **4c**. As discussed below (on RR spectra), the former seems to correspond with the T structure, while the latter two with the R structure.

The observed free-energy difference $\Delta\Delta G$, between ΔG_5 for base pentacoordination and ΔG_6 for base hexacoordination[8] (see Table II), amounting to ca. 3.8 kcal/mol for **4a** and ca. 4.5 kcal/mol for **4b** and **4c**, respectively, suggests that **3**·**4a** complexation is accompanied by additional strain of at least 0.8 kcal/mol compared to **4b** or **4c**. The observed additional strain supports the mechanism that **4a** affords the T structure, while **4b** and **4c** afford the R structure (see Figure 1).

Table II. Free-Energy Differences between Pentacoordination and Hexacoordination of Ferrous Porphyrins[a,b]

Fe^{II}·P	TPP	TPP	capped	MedPoc	tailed	gable	gable
L	DMI	HIm	1MI	1MI		DIM	DIP
$\Delta\Delta G^{b,c}$	5.6	−1.4	3.5	7.1	2.7	3.9	4.6

[a] All abbreviations are shown in Table I. [b] Calculated from K_5 and K_6 with $\Delta\Delta G = RT \ln K_5/K_6$, $T = 298$ K. [c] In kcal/mol.

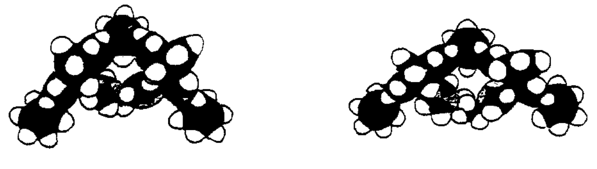
(a) (b)

Figure 1. T and R structures of artificial allosteric systems in the deoxy state. (a) gable·Fe^{II}_2·DIM, (b) gable·Fe^{II}_2·DIP.

Therefore, it may be concluded that the entropically favored endo,endo coordination of a series of dimeric bases of similar structures to the gable porphyrin·Fe^{II}_2 commplex provides an ideal T/R couple of stable pentacoordinate complexes with the least structures difference. The inductive effect of the introduced imidazole on the base binding is negligible as seen from the observed base association constants—log K_B (with TPP·Co^{II}) for 1MI and **4a** is 3.4 and 3.5, respectively.[5a] The model T/R couple allows detailed spectroscopic and thermodynamic and/or kinetic studies for T/R structure problem related to the observed allosteric effect.

Resonance Raman Spectra of Pentacoordinate T and R Complexes. The T/R structure was originally proposed for the deoxy Hb/oxy Hb couple where some deoxy subunits (originally in the T form) are assumed partly converted to the R form during the O_2 binding process. However, direct observation of this partial conversion seems extremely difficult, and usually the monomeric Hb subunit or Mb (myoglobin) is taken as a typical R conformer.[9] This T/R structure difference may be best described by the magnitude of out-of-plane movement of the central Fe^{II}, being 0.63 and 0.55 Å for deoxy T Hb and deoxy R Mb, respectively[10] (see Figure 2). This out-of-plane movement is believed to be caused by pulling by the fifth ligand connected with the Hb "F helix", which is again pulled by moderately strong subunit interaction at the subunit surface. As a result, strain in the T form seems to be distributed among the Fe^{II}–B stretching and the Fe out-of-plane movement.[11] However, the Fe^{II}–B stretching or the Fe^{II} out-of-plane movement, of course, highly depends also on the base structure (electron density, etc.), porphyrin structure, and local environment. Also it should be noted that the change in the Fe^{II}–B distance may not be sufficiently large in magnitude to be observed directly by X-ray, even when induced strain in Fe^{II}–B is reasonably large. For example, interestingly, deoxy T Hb and deoxy R Mb have the very close Fe^{II}–B distance, 2.0 Å for the α subunit and 2.2 Å for the β subunit in deoxy T Hb while 2.1

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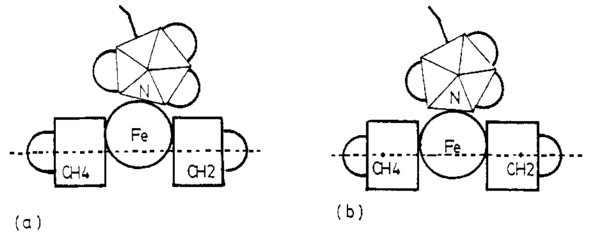

Figure 2. Local heme structures in (a) deoxy Hb (α) and (b) deoxy R Mb. See ref 11b.

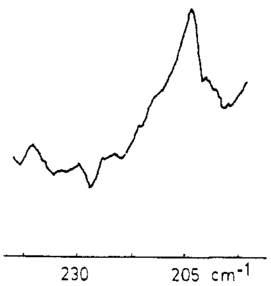

Figure 3. Low-frequency resonance Raman spectra of TPP-3CIm·$\mathrm{Fe^{II}}$ in benzene. The conditions are similar to that of gable·$\mathrm{Fe^{II}_2}$·DIM except [TPP-3CIm·$\mathrm{Fe^{II}}$] = 2 × 10^{-4} M.

± 0.1 Å in deoxy R Mb,[12] showing that the T/R structural effect is "hidden" among the other effects within experimental error. Therefore, it is really necessary to prepare a T/R couple of the same (or very similar) structure and environment and to have reliable spectroscopic methods to detect the T–R structure change, in order to gain further insights into structural and mechanistic features of the T/R problem in a *solution*.[13]

For this purpose, RR spectra of a series of pentacoordinate porphyrin $\mathrm{Fe^{II}}$·B complexes were investigated, since in a few examples RR spectroscopy has been properly applied to the T/R structure problem.[14] A novel tailed porphyrin with a short arm, **5**, was newly prepared as a new member of the T/R family, the size of which is rather small at the moment. The RR bands characteristic of $\mathrm{Fe^{II}}$–B stretching of pentacoordinate complexes[15] appeared in a 190–230-$\mathrm{cm^{-1}}$ region and are roughly classified into less stretched and more stretched groups. Two groups seem to correspond to R and T structures (see Table III and Figure 3), respectively. Especially interesting results were obtained for the present gable system (**3**·$\mathrm{Fe^{II}_2}$·**4**), where the short bridging base **4a** forms the deoxy complex with a RR band at 200 $\mathrm{cm^{-1}}$,[15a] while the longer arm bases **4b** and **4c** form the deoxy complexes with RR bands at 227 and 232 $\mathrm{cm^{-1}}$, respectively, strongly suggesting that the T and R complexes are formed depending on the magnitude of base pulling, just like the T/R couple of Hb. Out-of-plane displacement of the central $\mathrm{Fe^{II}}$ is also reflected in the observed RR shift in the 1640–1460-$\mathrm{cm^{-1}}$ region. However, contrary to the clear single peak for $\mathrm{Fe^{II}}$–Imd stretching, several peaks appeared in the 1640–1460-$\mathrm{cm^{-1}}$ region, making analysis more difficult.

Table III. $\nu_{\mathrm{Fe-N}}$ in Resonance Raman Spectra of Deoxy Hb and Mb and Model Systems[a,b]

$\mathrm{Fe^{II}}$·porphyrin	Raman obsd $\nu_{\mathrm{Fe-N}}$[b,c]
HbA[d,j]	
$\alpha_2\beta_2$	215
isolated α	223
isolated β	224
MbA[d,k]	222
$\mathrm{Fe^{II}}$·TpivPP·L[e]	
L, DMI	200
L, 2MI[l]	209
L, 1MI[f]	225
$\mathrm{Fe^{II}}$·PocPiv·L[g]	
L, DMI	193
L, 2MI	215
L, 1MI	227
$\mathrm{Fe^{II}}$·TPP–*n*-CIm[h,m]	
n, 3	204
n, 5	224
$\mathrm{Fe_2^{II}}$·gable·L[i]	
L, DIM	200
L, DIE	227
L, DIP	232

[a] All abbreviations are shown in Table I. X-ray Fe–N distances are shown in footnotes *j–m*. [b] Imidazole N. [c] In $\mathrm{cm^{-1}}$. [d] In pH 7.0, inositol hexaphosphate 1 mM, 10 °C, [heme] = 0.4 mM, ref 14g. [e] In $\mathrm{CH_2Cl_2}$, [heme] = 0.3 mM, ref 15g. [f] In solid state. [g] In $\mathrm{CH_2Cl_2}$ or benzene; 25 °C, ref 3p. [h] In benzene, [heme] = ca. 1 mM; room temperature, this work. [i] In benzene, [heme] = ca. 0.25 mM, room temperature, this work. [j] X-ray Fe–N distance, α = 2.0 Å and β = 2.2 Å. [k] X-ray Fe–N distance, 2.1 Å. [l] X-ray Fe–N distance, 2.095 Å. [m] The band at 201–202 $\mathrm{cm^{-1}}$ also appeared nearly the same intensity due to formation of the hexacoordinated species.

Table IV. O_2 and CO Affinities for Native and Artificial R and T Hemes

$\mathrm{Fe^{II}}$·porphyrin	K_{O_2}, $\mathrm{mm^{-1}}$[b]	K_{CO}, $\mathrm{mm^{-1}}$[b]	ref
Mb	1.43[c]	83.3[c]	1d
HbA, K_1	0.007[d,i]	10[c,j]	O_2: 1g
HbA, K_4	0.67	149	CO: 1i
HbA, isolated α	1.67[d]	400[d]	1d
HbA, isolated β	2.94[d]	625[d]	1d
$\mathrm{Fe^{II}}$·TPP·DMI		6.67	3q
$\mathrm{Fe^{II}}$·TPP·2MI		1.35	3q
$\mathrm{Fe^{II}}$·TpivPP·DMI	0.026	112	3q
$\mathrm{Fe^{II}}$·TpivPP·2MI	0.071		3q
$\mathrm{Fe^{II}}$·TpivPP·1MI[m]	2.04		3q
$\mathrm{Fe^{II}}$·PocPiv·DMI	0.083	14.9	3o
$\mathrm{Fe^{II}}$·PocPiv·1MI	2.78	667	3q
$\mathrm{Fe^{II}}$·TPP-3CIm[g]		0.4[f]	this work
$\mathrm{Fe^{II}}$·TPP-5CIm[g]		300[f]	this work
$\mathrm{Fe^{II}}$·gable·DIM[e]			5d
nonallosteric[k]		8.3[e]	5d
allosteric,[l] K_1		0.8[e]	5d
allosteric,[l] K_2		18[e]	
$\mathrm{Fe^{II}_2}$·gable·DIE[h]		158[f]	this work
$\mathrm{Fe^{II}_2}$·gable·DIP[h]		330[f]	this work

[a] All abbreviations are shown in Table I. [b] In toluene, 25 °C unless otherwise noted. [c] In 0.05 M bis(Tris) buffer, pH 7.4, 25 °C. [d] In bis(Tris) buffer, pH 7.4, DPG, 25 °C. [e] In DMF, 18 °C. [f] In DMF, 25 °C. [g] [heme] = 2 × 10^{-6} M, predominant intermolecular coordination at high concentration. [h] [$\mathrm{Fe^{II}_2}$·gable] = 5 × 10^{-6} M, [DIE or DIP] = 5 × 10^{-6} M. [i] K_1 and K_4 are sensitive to the conditions for the measurements. K_1 of 0.0144 and K_4 of 8.0 were observed in 0.1 M NaCl and 2 mM DPG (2,3-diphosphoglycerate), giving the largest K_4/K_1 of 556. K_1 of 0.077 and K_4 of 4.11 were reported in a NaCl free, DPG free 0.05 M bis(Tris) buffer, pH 7.4, 25 °C, giving a K_4/K_1 value of 53. Reference 1g. [j] K_1 of 15 and K_4 of 66 were reported in a DPG free, 0.1 M NaCl solution, pH 6.75, bis(Tris) buffer, giving a K_4/K_1 value of 4.4. Reference 1i. [k] [DIM] = 6.0 × 10^{-6} M, [$\mathrm{Fe^{II}_2}$·gable] = 6.0 × 10^{-6} M. [l] [DIM] = 7.7 × 10^{-5} M, [$\mathrm{Fe^{II}_2}$·gable] = 6.0 × 10^{-6} M. [m] In solid state.

On the basis of these results, the Fe–N stretching frequency in the RR spectrum is concluded to be valuable for the study of the T/R structure problem in solution.[16] It also confirms pen-

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(12) See ref 10.

(13) In an allosteric condition.

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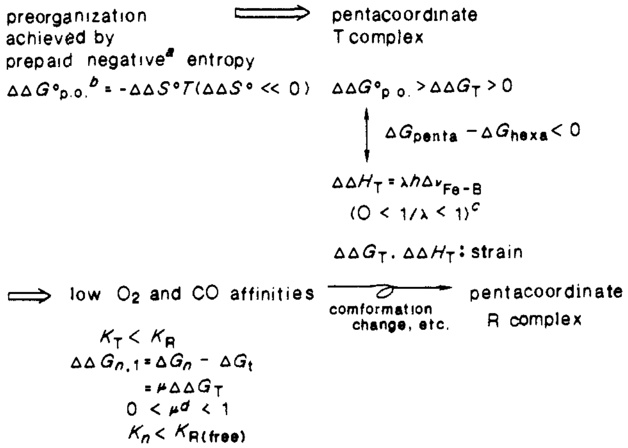
Table V. Relative CO and O_2 Affinities for T and R Fe^{II}·Porphyrin Couples Which Showed Appreciable Raman Shifts[a]

Fe^{II}·porphyrin	$\Delta\nu = \nu_R - \nu_T$, cm^{-1}	$K_{O_2}(R)/K_{O_2}(T)$	$K_{CO}(R)/K_{CO}(T)$
HbA, isolated $\alpha/(\alpha_2\beta_2)$	8	238	40
HbA, isolated $\beta/(\alpha_2\beta_2)$	9	420	62.5
HbA, allosteric		96 (50–556)[c] = K_4/K_1[b]	14.9 (4.4–14.9)[c]
Fe^{II}·TpivPP			
1MI/DMI	25	78	400[d]
Fe^{II}·PocPiv			
1MI/DMI	34	33	48
Fe^{II}·TPP-*n*-CIm			
−5/−3	20		750
Fe$^{II}_2$·gable			
DIP/DIM	32		40[e]
Fe$^{II}_2$·gable·DIM			
allosteric			23 = K_2/K_1[f]

[a] All abbreviations are shown in Table I. [b] Allosteric index of four sites. [c] See Footnote *i* and *j* in Table IV. [d] Reported *K* value for Fe^{II}·Piv$_3$-(5CIm)Por is used as K_R value. [e] Ratio for DIP/nonallosteric DIM couple. [f] Allosteric index of two sites.

Scheme I. Energetics of Cooperativity



[a] Prepaid during the preceding skeletal synthesis. [b] Including subunit interaction as the most important component. [c] A part of the strain is distributed in additional stretching of the Fe–B bond. [d] μ = magnitude of cooperativity.

tacoordination since tetracoordinate complexes showed no bands in the region of 200–240 cm^{-1}.[17] It also tells the magnitude of induced Fe^{II}–B stretching, characteristic of the T structure of porphyrin·Fe^{II} complexes including the present **3**·Fe$^{II}_2$·**4** complexes. Further differentiation between hexa- and pentacoordination was conveniently made by use of magnetic circular dichroism (MCD).[18] A typical example was seen for TPP·Fe^{II} complexes, in which the pentacoordinate complex with DMI showed a strong positive absorption at 435 nm, while the hexacoordinate complex with 1MI showed a very weak *negative* absorption at 425 nm. All of the gable complexes, **3·4a**, **3·4b**, and **3·4c**, gave pentacoordinate complexes predominantly based on MCD spectroscopy. Therefore, a conclusion may be drawn that our artificial allosteric system, pentacoordinate **3·4a**, takes the typical T structure in its deoxy state.

CO and O_2 Affinities of T and R Fe^{II}·Porphyrins and the Magnitude of Cooperativity. CO affinities of pentacoordinate Fe^{II}·porphyrin·B complexes **3·4b**, **3·4c**, and **5** were measured by following the characteristic absorptions of the CO complexes near 422 and 541 nm. The observed association constants, K_{CO}, together with reported K_{O_2} and K_{CO} for a series of pentacoordinate Fe^{II}·porphyrin·B complexes are listed in Table IV. Although the magnitudes of K_{O_2} and K_{CO} are spread over wide ranges,[19] 0.026–2.94 and 0.4–45400 mm^{-1}, respectively, there is a clear trend that for each T/R couple, always the R form has considerably higher O_2 and CO affinities than the T form, as shown in Table V. The trend confirms the concept of cooperativity[20a] based on the T/R reactivity–structure relationship, where T/R structures are independently confirmed by the Raman spectroscopy (loc. cit.). The observed CO affinity, K_{CO} = 0.8 and 330 mm^{-1} for **3a·4a** and **3a·4c**, respectively, further supports the previous conclusion that our artificial allosteric system, pentacoordinate **3a·4a** complex in the deoxy state takes the low-affinity T structure. As expected **3a·4b** behaves as the R complex similarly to **3a·4c** with a very minute contribution of strain due to the relatively short arm length of **4b**. The situation was typically reflected in the observed CO affinity of K_{CO} = 158 mm^{-1} at 7.1 × 10^{-6} M **3a** and 7 × 10^{-6} M **4b** in DMF at 25 °C, which is very close to but slightly smaller than **3a·4c**.

The observed ratios $K_{O_2}(R)/K_{O_2}(T)$ and $K_{CO}(R)/K_{CO}(T)$ now are spread over much narrower ranges than the *K* values themselves, 33–420 and 23–400, respectively. It may be interesting to see the magnitude of K_n/K_1, which determines the magnitude of cooperativity in a *n*-site allosteric system.[20b] In the native (Hb, *n* = 4) as well as the artificial (gable, *n* = 2) allosteric system, the R form operating as a subunit in the total allosteric system is *not so fully relaxed* as it should be in an isolated state. The magnitude of cooperativity is then to be defined by $(K_n/K_1)/(K_R/K_T)$. By taking the corresponding free-energy difference, a sketchy description on the energetics of cooperativity in a (native or artificial) allosteric system may be made (see Scheme I).

Experimental Section

Instruments and Apparatus. Resonance Raman spectra were recorded on a JRS-400T spectrometer (JEOL, Okazaki Institute for Molecular Science) with a spinning Pyrex cell (20 × 20 mm). An argon ion laser (Spectra-Physics 164-05, 5 W, Okazaki Institute for Molecular Science) was used for excitation at 4579 Å. Calibration of the Raman spectrometer was performed with the 217-cm^{-1} band of CCl_4.[21] Electronic spectra were measured with a Union SM-401 high-sensitivity spectrometer at 25 °C. CO determination was carried out with a gas chromatograph GC-4C (Shimadzu) equipped with a molecular sieve 13X (1.5 m).

Materials. Commercially available 1MI and 2MI (both from Nakarai Chemical Co.) were used after distillation under Ar or recrystallization from benzene, just before use. α,ω-(*N*,*N'*-diimidazolyl)-*n*-poly(methylene), Im$(CH_2)_m$Im (*m* = 1–3) was prepared by the reported procedure[22] with slight modification. Short tailed porphyrin, *meso*-[*o*-(3-(*N*-imidazolyl)propionamido)phenyl]triphenylporphyrin (3-tail TPP), **5**, was prepared from (o-aminophenyl)triphenylporphyrin and 3-(*N*-imidazolyl)propinyl chloride hydrochloride according to the literature.[23] Ferrous porphyrins (Fe$^{II}_2$·gable, Fe^{II}·3-tail-TPP, and Fe^{II}·5-tail-TPP) and others were prepared from corresponding ferric complexes by the reported procedure.[24] DMF was dried over CaH_2 and fractionally distilled at reduced pressure under Ar just before use. Benzene was dried with metallic Na and distilled on metallic Na under Ar.

Sample Preparation for the Raman Spectroscopy. All procedures were carried out in a Vacuum Atmospheres drybox, the internal atmosphere of which was constantly circulated through a MnO column (40 × 80 mm) settled inside to remove traces of oxygen[25] slowly penetrating in through the rubber gloves.

In a typical experiment, ferrous·gable porphyrin dissolved in benzene (ca. 5 × 10^{-4} M, 0.5 mL) and a benzene solution of an axial ligand (ca. 5 × 10^{-4} M, 0.5 mL) were placed in a spinning Pyrex cell (20 × 20 mm) equipped with a two-way high-vacuum stopcock. The atmosphere in the cell was replaced by Ar by a repeated evacuation–Ar (or an Ar–CO mixed gas of appropriate ratio) back-flushing (5 times) with external ice cooling. The spinning cell was sealed for further measurements.

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(18) Our preliminary results.

(19) See ref 3i and j.

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Measurements of Resonance Raman Spectra. The spinning cell was rotated at the rate of 1800 rpm.[26] The ferrous·gable porphyrin solution prepared as described above was excited by Ar laser irradiation at 4579 Å (80 mW) with a 458-nm pass filter. Resonance Raman spectra were recorded between 175 and 675 cm^{-1} (scanning speed, 2.5 cm^{-1} per min; time constant, 32 s; slit height, 10 mm; slit widths were kept at 400, 500, and 400 μm). Under the conditions, Raman spectra were satisfactory. However, at the low concentrations (ca. 10^{-5} M) of the ferrous porphyrins, intensities of the peaks in resonance Raman spectra were too weak to determine the band intensity of ν_{Fe-Im}.

CO Affinity Measurements. All procedures of sample preparation were carried out in a Vacuum Atmospheres drybox, the internal atmosphere of which was constantly circulated through a freshly prepared MnO column (20 × 40 mm) settled inside to remove traces of oxygen.

In a typical experiment, $Fe^{II}{}_2$·gable porphyrin dissolved in DMF (ca. 5×10^{-6} M, 2 mL) and a DMF solution of an axial ligand (0.5×10^{-3} M, 20 μL–0.2 mL) were placed in a 10-mm quartz cell equipped with a two-way high-vacuum stopcock.

The cell was then connected with a vacuum line, and the atmosphere in the cell was replaced by CO/Ar via repeated evacuation at 1×10^{-5} torr (with external cooling at −40 °C by use of a dry ice–acetone bath) followed by back-flushing of an Ar–CO gas mixture through the MnO column (8 × 100 mm). The stopcock was closed, and the solution was warmed up to 25 °C. Then, the electronic spectra of the solution were recorded.

The volume ratio of the Ar–CO gas mixture was determined by GC in the following conditions: 0.5 mL of gas mixture; molecular sieve 13X (1.5 m), He carrier (0.6 kg/cm^2), column temperature 30 °C.

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Registry No. 3a·4a, 97467-44-2; **3a·4b**, 104267-50-7; **3a·4c**, 104241-86-3; **5** (*i* = 2), 104241-87-4; **5** (*i* = 4), 75529-04-3; **5**·CO (*i* = 2), 104267-51-8; **5**·CO (*i* = 4), 75529-00-9; TPP·Fe^{II}·DMI, 72186-60-8; TPP·Fe^{II}·$(1MI)_2$, 54032-54-1; CO, 630-08-0.

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Unusual Magnetic Properties of the Adduct of Copper Chloride with 2-Phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-Oxide

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Abstract: A stable adduct was isolated from copper(II) chloride and the stable free radical 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide. The stoichiometry of the adduct is 1:2, and a crystal structure analysis has shown the copper ion to be four planar coordinated by two chlorine atoms and two oxygen (nitroxyl) atoms. The nitroxyl ligands are bound with a short Cu–O distance of 1.988 (1) Å. Magnetic measurements show that this material is in a doublet state from 30 to 300 K. At lower temperature a spin pairing process became operative. Crystal data: monoclinic, $P2_1/n$, a = 11.988 (4) Å, b = 10.878 (3) Å, c = 11.788 (4) Å, β = 106.14 (2)°, Z = 2.

Although a large number of relatively stable complexes of transition-metal ions with free radical have been described,[2] those classes which are sufficiently stable for isolation and characterization remain quite limited. Notable among these are the adducts of organometallic Lewis acid with dialkyl nitroxides.[3-12] Special interest has been devoted to those in which the metal ion is paramagnetic and the nitroxide metal coordinated.[4-13] These studies allow the opportunity of obtaining first hand information on metal–ligand interaction monitored by the magnetic coupling with the metal electrons.

Indeed several different behaviors have now been observed, ranging from a complete pairing of the unpaired electrons to an intermediate coupling, which can be either ferro-[9,12,14] or antiferromagnetic[5,7,10,13] depending on the nature of the metal ion and on the relative geometries of the magnetic orbitals on the radical and on the metal ion.

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