

stable; Dreiding models suggest it may well be the pseudoaxial conformation.

A linear thermal cheletropic fragmentation of 1-X-3,5-cycloheptadiene is predicted to occur by an axisymmetric¹⁰ conrotatory motion around the end carbons of the residual triene moiety.⁵ However, a nonlinear cheletropic fragmentation with disrotation is also allowed thermally.⁵ An equivalent analysis of the reverse addition of X to 1,3,5-hexatriene shows it should involve a linear approach of X with antarafacial bonding to the triene or a nonlinear superficial interaction.¹¹ Mock¹² has observed that thermal extrusion of SO₂ from stereoisomeric sulfones structurally analogous to **1** and **2** indeed occurs by the predicted axisymmetric conrotatory path. Thus, one would predict that if the photoinduced extrusion of CO from **1** and **2** should occur by the stereochemical mode opposite to that of the analogous ground-state system studied by Mock,¹² on the assumption that orbital symmetry is the controlling factor in this system,¹³ expulsion of CO along the axis of symmetry of these molecules on photoexcitation is predicted to be accompanied by disrotation in formation of the trienes, contrary to our experimental observation. Such a disrotatory extrusion of CO has been observed^{3,14,15,16} on photoexcitation of bridged bicyclic analogues of these dienones, which do not have any other viable alternative.

The possibility that these stereospecific decarbonylations are not concerted seems remote, since the *cis*- and *trans*-dienones are not interconverted and since **2** shows a clear preference for forming the *Z,Z,Z*-triene **4** rather than any of the other more stable triene isomers. For a nonlinear extrusion of CO, i.e., where CO does not depart along the axis of symmetry of the starting dienones, the selection rules⁵ would be reversed, consistent with the experimental observations, but there seems to be no compelling reason why such a course should be followed.¹⁹ The precise direction of departure of CO and analogous cheleofuges is not subject to experimental verification by an ordinary stereochemical experiment but perhaps could be analyzed theoretically. Other rationalizations revolve around considerations of the stereoelectronic control exercised by the n, π^* configuration of the excited state of these cycloheptadienones,^{3,13} and the rather remote possibility that the reaction is occurring on the ground-state potential surface following internal conversion from S₁. Finally, examination of Dreiding models indicates that in these twisted dienones the pseudoequatorial groups at C₂ and C₇ (H or CH₃) are nearly coplanar with the substituents (H in this instance) at C₃ and C₆, so that the conrotatory pathway (which amounts to little more than rehybridization) represents the path of least motion and would afford trienes in which these groups are on the same

side (i.e., *cis*) of the terminal C=C bonds; disrotation would cause much greater structural distortions. On this basis, one can rationalize the preferred formation of **4** from **2** if **2** is reacting primarily through the conformation in which the methyls occupy pseudoaxial positions.

In summary, we have observed that the photochemical extrusion of CO from cycloheptadienones **1** and **2** occurs stereospecifically by the same axisymmetric conrotatory mode seen in thermal extrusion of SO₂ from the analogous sulfones.¹² Since few reactions of this type have been studied,^{6,17} it remains to be seen what factors control the course of cheletropic fragmentations, particularly those induced by light.

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Registry No. **1**, 85236-00-6; **2**, 85236-01-7.

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Cooperative Dioxygen Binding by Cobalt(II) Gable Porphyrin in Homogeneous Solution

Iwao Tabushi* and Tomikazu Sasaki

*The Department of Synthetic Chemistry, Kyoto University
Sakyo-ku, Kyoto 606, Japan*

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The nature of cooperativity in protein action has been gradually elucidated in recent years. Cooperative dioxygen binding by hemoglobin, for example, is now reasonably understood as follows. The O₂ affinity of the T state is remarkably reduced due to intersubunit interaction, but the T state is converted to a high affinity form, R state, on O₂ binding. This conformation change induces the T → R conformation change in the remaining vacant binding sites of the tetrameric protein. Similarly, successive O₂ binding further drives the conformation change. Thus O₂ affinity finally approaches the "normal" value of myoglobin.¹ Among the events involved, the most important yet perhaps most difficult to understand seems to be the structural change of the "coupling site" that transfers the information for O₂ binding from one binding site to the other. In order to gain more insights into the mechanism of information transmission by the structural change of the coupling site, several attempts have been made to *mimic* the cooperative dioxygen binding by using solid metalloporphyrin^{2,3} or metalloporphyrin attached to a polymer.⁴ Although these systems showed large Hill coefficients, this is primarily due to multisite interaction.⁵ Mechanistic details on the molecular basis have not yet been clarified.

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Table I. Cooperative Parameters of O₂ Binding by Cobalt(gable)^a

diimidazolylmethane concn × 10 ⁻³ , M	0	2	7	15	20	112
$n \pm 0.1$ ^b	1.0	1.2	1.5	1.5	1.5	1.3
$P_{1/2} O_2$, mmHg	2300 ± 200	158 ± 10	160 ± 6	151 ± 19	143 ± 5	129 ± 10

^a Co^{II}(TPP) (*N*-methylimidazole): $n = 1.1 \pm 0.1$, $P_{1/2} = 56 \pm 7$ mmHg. Co^{II}(TPP) (diimidazolylmethane): $n = 0.9 \pm 0.1$, $P_{1/2} = 110 \pm 11$ mmHg. ^b Statistical error estimated from three to five independent runs.

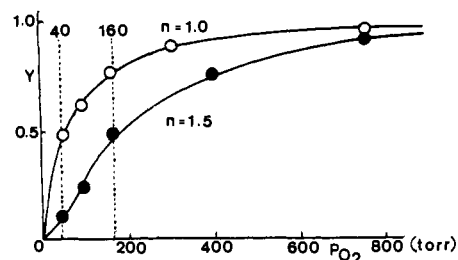
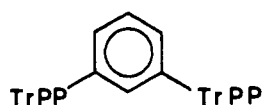


Figure 1. Partial O₂ pressure vs. fractional saturation: (O) TPP-Co^{II}(L); (●) (gable)Co^{II}(L); -20 °C, DMF. [Co^{II}₂(gable)] = 2.0 × 10⁻⁶ M, [L-L] = 15 × 10⁻³ M; [Co(TPP)] = 2.0 × 10⁻⁶ M, [L] = 0.04 M.

We report the first successful example of cooperative dioxygen binding by a dimeric metalloporphyrin in a homogeneous solution via a structural change-information transmission mechanism. Previously described "gable porphyrin" **1** was used in this study.



TrPP : triphenylporphyrinyl

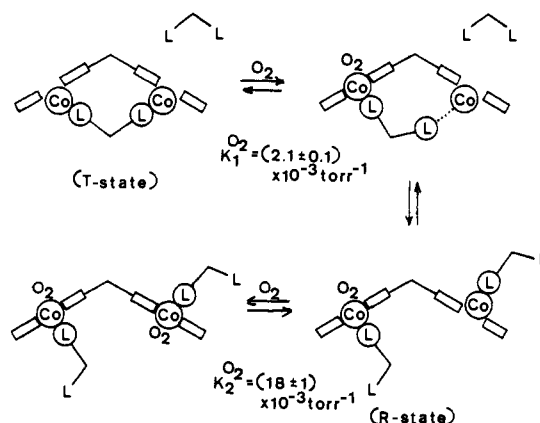
The bis(cobalt(II)) complex Co^{II}₂(gable) was prepared from 60 mg of CoCl₂ and 10 mg of gable porphyrin, **1** in 30 mL DMF under Ar. O₂ binding with this complex was studied in the presence of an appropriate ligand in DMF under N₂-O₂ at -20 °C, where concentrations of oxy- and deoxy-Co^{II}₂(gable) ligand were determined by the absorptions at 411 and 430 nm, respectively.

The Co^{II}₂(gable) complex binds various bases as the fifth ligand very similarly to Co(TPP).⁷ The base binding was measured in DMF at -20 °C by following the electronic spectrum change when the solution was titrated with the base. During the titration, clear isosbestic points were observed at 418 and 432 nm for Co(TPP) with 1-MeImd, 414 and 434 for Co(TPP) with (Imd)₂CH₂, 410 and 430 for Co₂(gable) with 1-MeImd, and 413 for Co₂(gable) with (Imd)₂CH₂. Association constants of imidazole complexes are as follows: (L)Co^{II}(TPP), (2.3 ± 0.5) × 10³ M⁻¹; (L-L)-Co^{II}(TPP), (3.0 ± 0.4) × 10³ M⁻¹; (L₂)Co^{II}₂(gable), (2.2 ± 0.6) × 10³ M⁻¹; ()Co^{II}₂(gable) (bridging), (4 ± 2) × 10⁶ M⁻¹, where

L = 1-methylimidazole and L-L = *N,N'*-diimidazolylmethane. The two Co^{II}(TPP) moieties of Co^{II}₂(gable) have practically the same association constants toward L (K_L), which are also nearly the same as K_L for monomeric Co^{II}(TPP), indicating that the simple base binds normally. Interestingly, a bridging bifunctional ligand showed an unusually large association constant toward Co^{II}₂(gable) but not for Co^{II}(TPP), indicating the two-site ligation of nearly additive energetics; $\Delta G_{LL}(\text{gable}) = 2\Delta G_{LL}(\text{TPP})$.⁸

The most interesting and noteworthy observation is that O₂ binding is clearly cooperative. Typical conditions: 3 mL of 2.0 × 10⁻⁶ M Co₂(gable) in DMF was equilibrated at -20 °C with 1 L of N₂-O₂ gas. Concentrations of the deoxy and oxy complexes

Scheme I. Schematic Representation of Cooperative O₂ Binding $K\{L\}Co^{II}(TPP) = (18 \pm 3) \times 10^{-3}$ torr⁻¹



were determined spectrophotometrically. Thus, as shown in Figure 1 the n value⁹ estimated is 1.5 under optimal conditions (see Table I), which was obtained by plotting $\log(Y/(1-Y))$ vs. $\log P_{O_2}$. The correlation coefficient was higher than 0.99. This is due to the retarded first O₂ binding and almost normal second O₂ binding as shown in Scheme I. This characteristic is similar to that observed for hemoglobin ($K_1 < K_2 < K_3 < K_4 \approx K(\text{isolated subunit})$).¹⁰ Estimated cooperative parameters are listed in Table I.

The presently observed cooperative O₂ binding seems to be interpreted by transition from a T state to an R state (Scheme I). In the absence of O₂ and in the presence of a (7–20) × 10⁻³ M concentration of the bridging bifunctional ligand, 98.0–99.9% of the Co^{II}₂(gable) should exist in a form of the bridged coordination deoxy state, which has reduced O₂ affinity (T state). When the first O₂ binds to the deoxy T state, Co^{II} prefers to take a planar coordination,^{11,12} resulting in the strain increase in the ligand-Co bond. This induced strain weakens the ligand-Co bond, enabling an available free ligand to form the monooxy R state (see Scheme I; $K_2^{O_2}/K_1^{O_2} = 8.6 \pm 0.3$).¹³ The present Co^{II}₂(gable) affords a chemical model of cooperative O₂ binding where O₂ transfer from Co^{II}₂(gable) to Co^{II}(TPP) by operating from 160 (lung) to 40 mmHg P_{O_2} (tissue) should amount to ca. 35% at -20 °C in DMF, similar to the hemoglobin-myoglobin transfer (35%).¹⁴

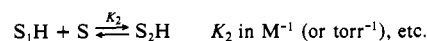
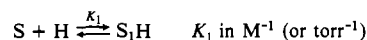
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This kind of treatment is frequently seen in the literature; see: (a) Lehn, J.-M.; Simon, J. *Helv. Chim. Acta* **1977**, *60*, 141–151. (b) Rebek, J., Jr.; Wattlely, R. V.; Costello, T.; Gadwood, R.; Marshall, L. *Angew. Chem.* **1981**, *93*, 584–585 (this describes the interesting activation driven by the intramolecular conformation change in close correlation with allostery). Numerical values of K_1 and K_2 were obtained by computer simulation.

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