relevant: (1) Given the substitutional and valence electronic characteristics of the reactants, electronic coupling by orbital overlap between donor and acceptor sites is presumably weak, as in a typical outer-sphere electron-transfer.¹² (2) Since electron and proton transfer are inherently coupled, there is no real charge-transfer component to the reaction, and so no significant contribution from outer-sphere reorganization (medium vibrations) is expected. (3) Because of the high frequency vibrations involved $\nu_{\rm OH} \sim 3600 \text{ cm}^{-1}, \nu_{\rm Ru=0} \sim 795 \text{ cm}^{-1}$, and the low thermal activation energy, the reaction must proceed largely from the v =0 level of the ν_{OH} mode and hence involve vibrational tunneling. In this sense, with regard to what are most probably the critical vibrational modes, the reaction occurs in the low-temperature (quantum mechanical) limit.¹³⁻²¹ (4) The case reported here may be a limiting example of H-atom (proton-coupled, 1-electron) transfer where the distinguishing feature is weak electronic coupling between the electron donor and acceptor sites.

Our results may have important implications for a number of redox related observations including the electron-transfer chemistry of metal-oxo compounds, the interpretation of kinetic isotope effects, and the general role of proton-coupled electron transfer in both chemical and biological systems.

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An Iron(III)-Porphyrin Complex with a Vinylidene Group Inserted into an Iron-Nitrogen Bond: Relevance to the Structure of the Active Oxygen Complex of Catalase

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Various hemoproteins including cytochrome P450, catalases, and peroxidases catalyze the oxidation of organic compounds by two-electron oxidants such as hydroperoxides. The reactions of catalases and peroxidases with these oxidants lead to intermediate complexes called compounds I and II which retain, respectively, two and one oxidizing equivalents above the native ferrihemoproteins.¹ Though the structures of these intermediates are not



b 1 " = TTP

definitely established, compound II is generally believed to be an iron(IV) complex with an oxo (A in Scheme I) or OH exogenous ligand.² The structure of compound I which retains one oxidizing equivalent above compound II is even less known. The relative stability of horseradish peroxidase (HRP) compound I has allowed its study by various spectroscopic methods³ which support an iron(IV) [porphyrin π -cation radical] structure.⁴ There are less spectroscopic data⁵ available for catalase compound I (CAT I) probably because of its unstability. However, a similar iron(IV) [porphyrin π cation radical] structure has been proposed for CAT I taking into account the analogy of its electronic spectrum with those of cobalt porphyrin π cation radicals.⁴

The porphyrin-iron-carbene complexes PFe^{IV}==CRR' ↔ PFe^{II} \leftarrow CRR', which we have recently synthesized,⁶ are carbon analogues of the porphyrin-iron-oxo species A possibly present in compounds II. Upon one-electron oxidation of the vinylidene-iron complex⁷ Fe(TPP)[C=C(p-ClC₆H₄)₂] (1a) by CuCl₂, the stable complex Fe(TPP)[C=C(p-ClC₆H₄)₂]Cl (2a) was isolated as a crystalline solid.⁸ This complex, which exhibits a visible spectrum strikingly similar to that of CAT I, can be considered formally as a carbon analogue of CAT I (Scheme I).⁸

We present in this paper an X-ray structure analysis of the complex $Fe(TTP)[C=C(p-ClC_6H_4)_2]Cl(2b)$ which shows that

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⁽⁷⁾ TPP and TTP are, respectively, the dianions of meso-tetraphenylporphyrin and meso-tetra-p-tolylporphyrin.

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Figure 1. ORTEP drawing of the molecular structure of complex 2b. The *p*-tolyl groups in meso positions on the porphyrin ligand have been omitted for clarity.

the vinylidene entity is actually inserted between the iron atom and the nitrogen of one pyrrole ring of the porphyrin. From these results, we suggest a similar Fe^{III}-O-N bridged structure for CAT I which takes into account its spectral properties and specific reactivity.

Complex 2b⁹ has been prepared by oxidation of the vinylidene complex $Fe(TTP)[C=C(p-ClC_6H_4)_2]$ (1b) by CuCl₂ according to the method described for complex 2a.8a The UV-visible and EPR spectra of complexes 2a and 2b are identical. Single crystals of the latter complex suitable for an X-ray structure determination were obtained by slow evaporation of its 1,2-dichloroethane solutions.¹⁰ In this compound (Figure 1) the terminal carbon atom of the vinylidene moiety is bonded both to the iron atom and the pyrrole nitrogen N_4 , the corresponding bond distances being 1.914 (7) and 1.387 (6) Å, respectively. The iron(III) atom is fivecoordinate. As indicated by the large Fe---N₄ separation of 2.520 (8) Å, the metal atom is not linked to the pyrrole nitrogen N_4 but only to the three pyrrole nitrogens N_1 , N_2 , and N_3 of the macrocycle, a chlorine atom, and the carbon atom C_1 of the vinylidene group. The mean value of the three $Fe-N_P$ bond distances is 1.990 (5) Å, whereas the Fe-Cl₃ bond length is 2.290 (2) Å.¹¹ The four pyrrole nitrogens are approximately coplanar.¹² The iron atom is displaced out of this (4N) mean plane by 0.3 Å toward the chlorine ligand. Although the individual pyrrole rings are almost planar, the angles between the (4N) mean plane

and the pyrrole rings N_1-N_4 are 6.0, 14.3, 9.8, and 36.4°, respectively. The N_4 pyrrole is thus tilted toward the metal, while the other pyrrole rings remain almost parallel to the (4N) mean plane. The iron atom and the N_4 pyrrole nitrogen are coplanar with the vinylidene C_1 , C_2 , CV_1 , and CV_7 carbon atoms. This plane is almost perpendicular to the (4N) mean plane (91.0°) and contains also the pyrrole nitrogen N_2 . The two phenyl rings of the vinylidene moiety are almost orthogonal (83.8°).

Such a highly distorted five-coordinate geometry of the metal center is without precedent in the chemistry of iron porphyrins.^{8c} The results related to structure of the porphyrin macrocycle present in **2b** are, however, very similar to those previously described for Ni(II)–^{13a,b} Co(III)–^{13c,d} and Zn(II)–porphyrin complexes.^{13a} In this regard, the structures of the Ni–TPP complexes having inserted the CHCOOC₂H₅ carbene^{13b} or the NSO₂-*p*-CH₃C₆H₄ nitrene^{13a} in a Ni–N bond are very similar to that of complex **2b**.

These data suggest that upon one-electron oxidation of complexes 1, the electrophilic vinylidene ligand is no longer stabilized enough by the iron in the ferric state and requires the nucleophilic assistance of one pyrrole nitrogen atom leading to the formation of the more stable σ -Fe^{III} complexes 2 (Scheme I).

The visible spectra of the crystals and their solutions in various solvents (e.g., C_6H_6 , CH_2Cl_2) are identical, ruling out the existence of two different structures in these conditions. Moreover, upon treatment by CF₃CO₂H, the cleavage of the σ bond of complexes 2 together with their demetalation leads to the corresponding *N*-vinylporphyrins.¹⁴ A similar reaction had been previously described for the Ni(TPP)(CHCOOC₂H₅)^{13b} and Co(TPP)(CH-COOC₂H₅)Cl^{13c} complexes.

Two structures now appear compatible with the spectroscopic data presently available for catalase compound I: the previously proposed Fe^{IV}=O [porphyrin π cation radical] one⁴ and a new structure similar to that of complex 2b, with an oxygen atom inserted into an iron(III)-N bond of the heme (structure B in scheme I), that we propose²² on the basis of the great similarity of the electronic spectra and magnetic susceptibility of CAT I and complex 2b.^{8a} In this structure, the active oxygen atom, formally an oxene, coming from the hydroperoxide, plays the same role as the carbene moiety in complexes 2. Moreover, structure B would explain some of the specific reactivities of CAT I. It has been pointed out that CAT I and peroxidase compounds I display different chemical reactivity;^{15,17} for instance nitrite ions are oxidized by CAT I via a two-electron process^{16a,b} and by HRPI via two successive one-electron processes.^{16c,d} Moreover, CAT I contrary to HRPI is able to oxidize alcohols.¹⁷ It has been proposed¹⁵ that CAT I contains only one reactive oxidizing center, whereas peroxidase compounds I contain two of them. For instance, cytochrome c peroxidase I has been described as an iron(IV) complex with a free radical on an amino acid residue¹⁸ and HRP I as an iron(IV) complex of a porphyrin π -cation radical.^{3,4} Structure B may account for a unique reactive center in CAT I, able to oxidize nitrite ions, H_2O_2 , or alcohols via two-electron processes.¹⁹

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⁽¹²⁾ The deviations from the four porphinatonitrogen mean plane are +0.05 Å for N₁ and N₃ and -0.05 Å for N₂ and N₄. As indicated in the text the iron atom is displaced by 0.30 Å from this (4N) mean plane toward the chlorine atom but only by 0.25 Å from the mean plane of the 24-atom core of the porphyrin.

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The active oxygen complexes formed upon reaction of ferric hemoproteins of ferriporphyrins with single oxygen donors such as iodosylarenes have been described as $Fe^{V}=0$,^{8b,15,20}, $Fe^{IV}=0$ (porphyrin π cation radical),^{3,4,15} or $Fe^{IV}R$. (R being an amino acid residue)^{3b,18} complexes. In some cases, the occurrence of structure B which involves the iron in a peculiar coordination environment but in its usual ferric state should also be considered.²¹

(19) Involving the electrophilic reaction of the oxygen atom of CAT I driven by the regeneration of the Fe–N bond, which can be schematically

$$N - Fe \xrightarrow{\mathbf{m}}_{0} N + H \xrightarrow{\mathbf{x}}_{0} 0 \xrightarrow{\mathbf{r}}_{0} H \xrightarrow{\mathbf{r}}_{0} N \xrightarrow{\mathbf{r}}_{0} \xrightarrow{\mathbf{r}}_{0} H \xrightarrow{\mathbf{r}}_{0} \xrightarrow{\mathbf{r}}$$

viewed as

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Site Symmetry and the Framework Group

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In a recent article in this journal, Pople proposed the useful concept of a *framework* group¹ in order to specify molecular symmetry more completely than is accomplished by using only point group notation. This formalism appears especially useful for machine computations of structures from the symmetry notation and vice versa. The purpose of this communication is to recast the formalism in terms of site symmetry groups.² There are several advantages to this: (a) The subsets of atoms can be easily shown to be mutually exclusive, since the site symmetry and interchange groups share no common generators.^{2b} (b) Pople's k values are simply the order of the interchange groups, which, in turn, are the orders of the full point groups divided by those of the site symmetry groups. (c) The site symmetry terminology is already in the literature, thus avoiding the introduction of the new terminology (the O, X, etc., labels). (d) Most importantly, computational advantages are obtained in the construction of linear combinations of basis functions. These are obtained by the successive application of the site symmetry and interchange group projection operators.2b

The site symmetry group, G_s , of a site in a molecule is the group defined by the symmetry elements which pass through that site. The interchange group, G_I , is the group which interchanges the equivalent sites and is defined by the generators of the full group which are not included in the site symmetry.^{2b} Table I lists the site symmetry and interchange groups for some selected systems. Both the site symmetry and the interchange groups for a position can be as high as the full point symmetry or as low as C_1 . The generators of the point group appear in one or the other of these, but they cannot appear in both. Thus, subsets of atoms having

 Table I.
 Site Symmetry and Interchange Groups for Some

 Selected Systems³
 Selected Systems³

point group	moleculea	ligand	G _s	G_I	
C _{3U}	AX ₃	x	Cs	<i>C</i> ₃	
	AX ₃ Y	Y	C_{3v}	C_{i}	
C_{4v}	AX_4	X	C_s	C_4	
	AX₄YZ	Y(Z)	C_{4v}	C_1	
C_{nv}	AX_n	Х	C_s	C_n	
D_{2h}	$AX_2Y_2Z_2$	X(Y,Z)	C_{2v}	C_2	
D_{2d}	AX_2Y_2	X(Y)	C_s	D_{2}	
D_{3h}	AX ₃	Х	$C_{2\nu}$	C_3	
	AX_2Y_2	Y	C_{3v}	C_2	
D_{3d}	AX_6	Х	C_s	S_6	
D_{4h}	AX ₄	Х	C_{2v}	C_4	
	AX_4Y_2	Y	$C_{4\nu}$	C_{2}	
D_{6h}	X ₆	X	C_{2U}	C_6	
T_d	AX₄	Х	$C_{3\nu}$	S_{4}	
$\tilde{O_h}$	AX ₆	Х	$C_{4\nu}$	S_4	
$D_{\infty h}$	\mathbf{X}_{2}	X	$C_{\infty v}$	C_i	

^a The A atom in each case has the full point symmetry as its site symmetry and C_1 as its interchange symmetry.

Table II. Site Symmetries and k Values

group	site symmetries	k values	
$\overline{C_1}$	<i>C</i> ₁	1	
C_s	C_{s}, C_{1}	1, 2	
C_i	C_i, C_1	1, 2	
C_n	C_n, C_1	1, <i>n</i>	
C_{2v}	$C_{2\nu}, C_s, C_s', C_1$	1, 2, 2, 4	
C_{nv} (n odd)	$C_{nv}, \tilde{C}_{s}, \tilde{C}_{1}$	1, n, 2n	
C_{nv} (<i>n</i> even)	C_{nv}, C_s, C_s', C_1	1, n, n, 2n	
C_{nh}	C_{nh}, C_n, C_s, C_1	1, 2, n, 2n	
S_{2n}	S_{2n}, C_n, C_1	1, 2, 2 <i>n</i>	
D_n (n odd)	$D_{n}, C_{n}, C_{2}, C_{1}$	1, 2, n, 2n	
D_n (<i>n</i> even)	$D_{n}, C_{n}, C_{2}, C_{2}, C_{1}$	1, 2, n, n, 2n	
D_{nd}	$D_{nd}, C_{nv}, C_2, C_8, C_1$	1, 2, 2n, 2n, 4n	
D_{2h}	$D_{2h}, C_{2v}, C_{2v}, C_{2v}', C_{2v}'', C_{s}$	1, 2, 2, 2, 4, 4, 4, 8	
	C_{s}', C_{s}'', C_{i}		
D_{nh} (n odd)	$D_{nh}, C_{nv}, C_{2v}, C_{s}, C_{s}', C_{1}$	1, 2, n, 2n, 2n, 4n	
D_{nh} (<i>n</i> even)	$D_{nh}, C_{nv}, C_{2v}, C_{2v}', C_{s}$	1, 2, n, n, 2n, 2n, 2n, 4n	
	C_{s}', C_{s}'', C_{1}		
Т	T, C_3, C_2, C_1	1, 4, 6, 12	
T_d	$T_d, C_{3\nu}, C_{2\nu}, C_{s}, C_1$	1, 4, 6, 12, 24	
T_h	$T_{h}, C_{3}, C_{2}v, C_{s}, C_{1}$	1, 8, 6, 12, 24	
0	O, C_4, C_3, C_2, C_1	1, 6, 8, 12, 24	
O_h	$O_h, C_{4\nu}, C_{3\nu}, C_{2\nu}, C_{s}$	1, 6, 8, 12, 24, 24, 48	
	C_{s}', C_{1}		
Ι	$I, C_{5}, C_{3}, C_{2}, C_{1}$	1, 12, 20, 30, 60	
I _h	$I_{h}, C_{sv}, C_{3v}, C_{2v}, C_{s}, C_{1}$	1, 12, 20, 30, 60, 120	
$C_{\infty v}$	$C_{\infty U}, C_s$	1, ∞	
$D_{\infty h}$	$D_{\infty h}, C_{\infty v}, C_{2v}, C_{s}$	1, 2, ∞, ∞	

Table III. Correlation of C_{3v} and S_4 with T_d



different site symmetries are mutually exclusive.

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⁽³⁾ Reference 2d, p 218.

Recasting the framework group in terms of the site symmetry groups amounts to using the site symmetry labels instead of the O, C_n, X , etc., labeling used by Pople. The O label is always replaced by the label of the point group, and the X label always by C_1 . The other labels depend upon which symmetry elements pass through the points. Table II presents Table I of ref 1 in the new notation. The framework notation for a particular molecule can be derived by the obvious substitutions. For example, a tetrahedral XY₄ molecule would be classified $T_d(T_d(X), 4C_{3p}(Y)]$