The active oxygen complexes formed upon reaction of ferric hemoproteins of ferriporphyrins with single oxygen donors such as iodosylarenes have been described as $\mathrm{Fe^{V}{=}O}$,[8b,15,20] $\mathrm{Fe^{IV}{=}O}$ (porphyrin π cation radical),[3,4,15] or $\mathrm{Fe^{IV}R\cdot}$ (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]

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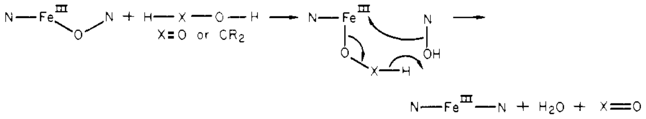
(19) Involving the electrophilic reaction of the oxygen atom of CAT I driven by the regeneration of the Fe–N bond, which can be schematically



viewed as

(20) Groves, J. T.; McClusky, G. A.; White, R. E.; Coon, M. J. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 154.

(21) The formation of a species exhibiting a CAT-I-like visible spectrum has been recently reported upon reaction of iron(III) octaethylporphyrin chloride with 2,6-dimethyliodosylbenzene: Chang, C. K.; Kuo, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3413.

(22) It has been previously suggested that metal (M) insertion into *N*-oxide porphyrins could lead to complexes with a M–O–N moiety: Bonnet, R.; Ridge, R. J.; Appelman, E. H. *J. Chem. Soc., Chem. Commun.* **1978**, 310. Possible involvement of M–O–N structures has been proposed by: Callot, H. J. and Schaeffer, E. *Nouveau J. Chim.* **1980**, *4*, 307.

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 group*[1] 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 different site symmetries are mutually exclusive.

Table I. Site Symmetry and Interchange Groups for Some Selected Systems[3]

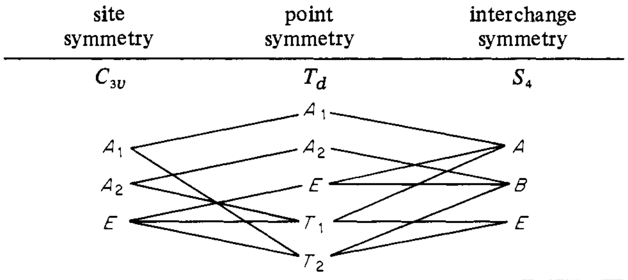
point group	molecule[a]	ligand	G_s	G_I
C_{3v}	AX_3	X	C_s	C_3
	AX_3Y	Y	C_{3v}	C_1
C_{4v}	AX_4	X	C_s	C_4
	AX_4YZ	Y(Z)	C_{4v}	C_1
C_{nv}	AX_n	X	C_s	C_n
D_{2h}	$AX_2Y_2Z_2$	X(Y,Z)	C_{2v}	C_2
D_{2d}	AX_2Y_2	X(Y)	C_s	D_2
D_{3h}	AX_3	X	C_{2v}	C_3
	AX_2Y_2	Y	C_{3v}	C_2
D_{3d}	AX_6	X	C_s	S_6
D_{4h}	AX_4	X	C_{2v}	C_4
	AX_4Y_2	Y	C_{4v}	C_2
D_{6h}	X_6	X	C_{2v}	C_6
T_d	AX_4	X	C_{3v}	S_4
O_h	AX_6	X	C_{4v}	S_4
$D_{\infty h}$	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
C_1	C_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, n
C_{2v}	C_{2v}, C_s, C_s', C_1	1, 2, 2, 4
C_{nv} (n odd)	C_{nv}, C_s, C_1	1, n, $2n$
C_{nv} (n 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, $2n$
D_n (n odd)	D_n, C_n, C_2, C_1	1, 2, n, $2n$
D_n (n 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_s, C_1	1, 2, $2n$, $2n$, $4n$
D_{2h}	D_{2h}, C_{2v}, C_{2v}', C_{2v}'', C_s, C_s', C_s'', C_1	1, 2, 2, 2, 4, 4, 4, 8
D_{nh} (n odd)	D_{nh}, C_{nv}, C_{2v}, C_s, C_s', C_1	1, 2, n, $2n$, $2n$, $4n$
D_{nh} (n even)	D_{nh}, C_{nv}, C_{2v}, C_{2v}', C_s, C_s', C_s'', C_1	1, 2, n, n, $2n$, $2n$, $2n$, $4n$
T	T, C_3, C_2, C_1	1, 4, 6, 12
T_d	T_d, C_{3v}, C_{2v}, C_s, C_1	1, 4, 6, 12, 24
T_h	T_h, C_3, C_{2v}, C_s, C_1	1, 8, 6, 12, 24
O	O, C_4, C_3, C_2, C_1	1, 6, 8, 12, 24
O_h	O_h, C_{4v}, C_{3v}, C_{2v}, C_s, C_s', C_1	1, 6, 8, 12, 24, 24, 48
I	I, C_5, C_3, C_2, C_1	1, 12, 20, 30, 60
I_h	I_h, C_{5v}, C_{3v}, C_{2v}, C_s, C_1	1, 12, 20, 30, 60, 120
$C_{\infty v}$	$C_{\infty v}$, 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



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 XY_4 molecule would be classified $T_d[T_d(\mathrm{X}),4C_{3v}(\mathrm{Y})]$

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(1) J. A. Pople, *J. Am. Chem. Soc.*, **102**, 4615 (1980).

(2) (a) R. L. Flurry, Jr., *Int. J. Quantum Chem.*, **S6**, 455 (1972); (b) *Theoret. Chim. Acta*, **31**, 221 (1973); (c) *J. Chem. Ed.*, **53**, 554 (1976); (d) "Symmetry Groups: Theory and Chemical Applications", Prentice-Hall, Englewood Cliffs, NJ, 1980.

(3) Reference 2d, p 218.

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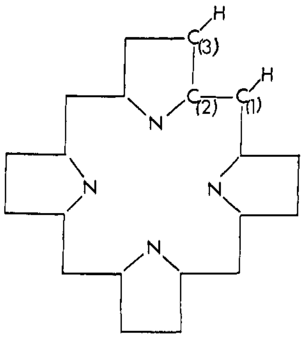
(the notation $T_d[T_d(X),C_{3v}(Y)]$ is actually sufficient). The notation for CH_2F_2 would be $C_{2v}[C_{2v}(C),C_s(H),C_s'(F)]$. That for the porphine dianion (**1**) would be $D_{4h}[C_{2v}(N),C_{2v}'(C(1)H),C_s(C(2),C(3)H)]$. Tables II–V of ref 1 have their original meaning with the obvious substitution of the new definitions.



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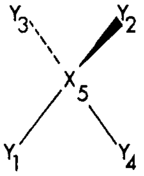
For an illustration of the computational utility of site symmetry and interchange groups, consider the construction of symmetry adapted functions from an s and p basis set on each atom of the tetrahedral XY_4 system (**2**). Let the reference Cartesian axes



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be parallel to the C_2 axes. Call the basis functions s_i, x_i, y_i, and z_i. The orientation of the x_i on the Y atoms should be such that they are interchanged by the operations of the interchange symmetry group and similarly for the y_i and z_i. The site symmetry of X is the full T_d and that for Y_i is C_{3v}. The respective interchange groups are C_1 and S_4. A correlation diagram[4] of C_{3v} and S_4 with T_d is useful. This is given in Table III. This tells us that, for example, a function transforming as the A_1 representation in the C_{3v} site symmetry and as E under the interchange spans the T_2 representation of T_d.

For the X atom, s_5 transforms as A_1 within T_d, while x_5, y_5, and z_5 together transform as T_2. For Y_1, s_1 transforms as A_1, while x_1, y_1, and z_1 span $A_1 + E$. By using the projection operators, P^Γ, from C_{3v}, the symmetry adapted combinations of x_1, y_1, and z_1 are

$$P^{A_1}x_1 = (1/\sqrt{3})(x_1 + y_1 + z_1) \equiv a_1 \qquad (1)$$

$$P^{E}x_1 = (1/\sqrt{6})(2x_1 - y_1 - z_1) \equiv e_1 \qquad (2)$$

$$P^{E\prime}x_1 = (1/\sqrt{2})(y_1 - z_1) \equiv p_1 \qquad (3)$$

(where eq 2 and 3 are the two orthogonal components of the E function.) The symmetry adapted functions in T_d can be obtained by applying the appropriate S_4 projection operators to s_1, a_1, e_1, and p_1. We have for the A_1 functions

$$P^{A}s_1 = N(s_1 + s_2 + s_3 + s_4) \equiv \lambda_1^{\mathrm{A}_1} \qquad (4)$$

$$P^{A}a_1 = N(a_1 + a_2 + a_3 + a_4) = N(x_1 + x_2 + x_3 + x_4 + y_1 + y_2 + y_3 + y_4 + z_1 + z_2 + z_3 + z_4) \equiv \lambda_2^{A_1} \qquad (5)$$

where the N's are normalizing constants. Several combinations are possible for the degenerate E, T_1, and T_2 functions. Unique combinations should be chosen. The combinations EB for E, EE for T_1, and A_1B and EE for T_2, where the first listed representation is from the site symmetry and the second from the interchange, are suitable choices. The two components of the E representation of S_4 acting on the same component of the E from C_{3v} give the T_1 and T_2 functions. We have for one component of the E functions

$$P^{B}e_1 = N(e_1 - e_2 + e_3 - e_4) = N[2(x_1 - x_2 + x_3 - x_4) - (y_1 - y_2 + y_3 - y_4) - (z_1 - z_2 + z_3 - z_4)] \equiv \lambda^{E} \qquad (6)$$

For one component of the T_1 function

$$P^{E}e_1 = N(e_1 - e_3) = N[2(x_1 - x_3) - (y_1 - y_3) - (z_1 - z_3)] \equiv \lambda^{T_1} \qquad (7)$$

And for one component of each of the T_2 functions

$$P^{\mathrm{B}}s_1 = N(s_1 - s_2 + s_3 - s_4) \equiv \lambda_1^{T_2} \qquad (8)$$

$$P^{B}a_1 = N(a_1 - a_2 + a_3 - a_4) = N(x_1 - x_2 + x_3 - x_4 + y_1 - y_2 + y_3 - y_4 + z_1 - z_2 + z_3 - z_4) \equiv \lambda_2^{T_2} \qquad (9)$$

$$P^{E}e_1N(e_2 - e_4) = N[2(x_2 - x_4) - (y_2 - y_4) - (z_2 - z_4)] \equiv \lambda_3^{T_2} \qquad (10)$$

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[4] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955, p 122.

Radical Anion of 1,1-Difluoroethylene. EPR Evidence for a Perpendicular Geometry

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Fluorine substitution is known to have a profound effect on the geometry and electronic structure of alkyl radicals.[1-3] Also, it has been demonstrated that increasing fluorination of the benzene and pyridine radical anions brings about a π^*–σ^* crossover in the electronic structure of these radicals.[4,5] Since previous work has provided strong evidence that the tetrafluoroethylene radical anion is a σ^* radical,[6] we have sought to generate the 1,1-difluoroethylene radical anion in the solid state and compare the structures of these two radicals. We find that the EPR spectrum of $CF_2{=}CH_2^-$ can be uniquely interpreted in terms of a 90° twisted (perpendicular) molecular geometry, the unpaired electron occupying an orbital which can be designated as σ^* (or π'^*)[7] for the CF_2 group and π for the CH_2 group.

The lower spectrum (c) in Figure 1 obtained from a γ-irradiated solution of $CF_2{=}CH_2$ in methylcyclohexane-d_{14} (MCHD) glass shows a pair of broad anisotropic features positioned just inside the lines of atomic hydrogen. Careful studies at 77 K established that these signals were produced to the exclusion of the narrow singlet from the matrix-trapped electron[8] for 1,1-difluoroethylene solutions in both MCHD and 2-methyltetrahydrofuran[9] glasses, thereby proving that these outer features result from electron capture by the solute. Thus, the features are assigned to the outer lines of a triplet spectrum resulting from hyperfine interaction with the two fluorines[10] in $CF_2{=}CH_2^-$, the center line being

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[9] McNeil, R. I.; Ph.D. thesis, University of Tennessee, 1978.

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