J. Am. Chem. Soc. 1981, 103, 2899–2901

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 $\nu_{OH} \sim 3600$ cm^{-1}, $\nu_{Ru=O} \sim 795$ 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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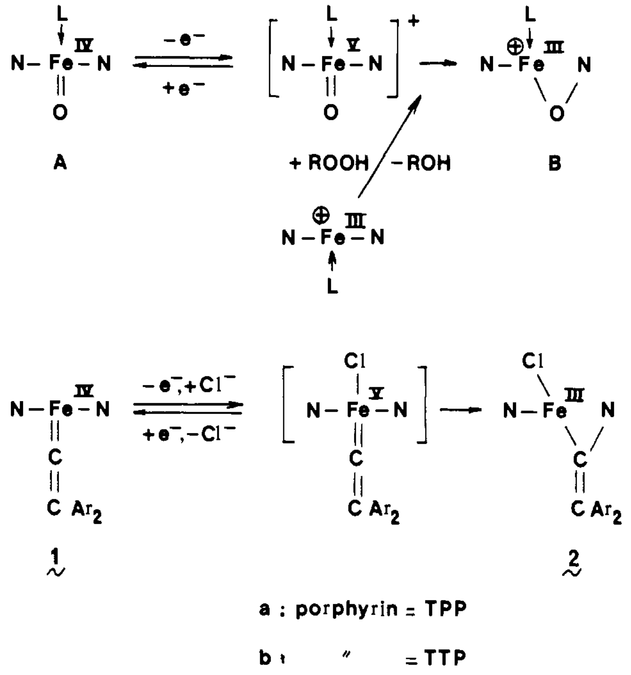
Various hemoproteins including cytochrome P450, catalases, and peroxidases catalyze the oxidation of organic compounds by two-electron oxidants such as hydroperoxides. The reactions of catalases and peroxidases with these oxidants lead to intermediate complexes called compounds I and II which retain, respectively, two and one oxidizing equivalents above the native ferrihemoproteins.[1] Though the structures of these intermediates are not 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 methods[3] which support an iron(IV) [porphyrin π-cation radical] structure.[4] There are less spectroscopic data[5] 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]

Scheme I



The porphyrin–iron–carbene complexes $PFe^{IV}{=}CRR' \leftrightarrow PFe^{II} \leftarrow CRR'$, 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 complex[7] $Fe(TPP)[C{=}C(p\text{-}ClC_6H_4)_2]$ (**1a**) by $CuCl_2$, the stable complex $Fe(TPP)[C{=}C(p\text{-}ClC_6H_4)_2]Cl$ (**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 $Fe(TTP)[C{=}C(p\text{-}ClC_6H_4)_2]Cl$ (**2b**) which shows that

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[6] Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681 and references cited therein.

[7] TPP and TTP are, respectively, the dianions of *meso*-tetraphenylporphyrin and *meso*-tetra-*p*-tolylporphyrin.

[8] (a) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6437. (b) Mansuy, D.; Chottard, J. C.; Lange, M.; Battioni, J. P. *J. Mol. Catal.* **1980**, *7*, 215. (c) The magnetic susceptibility and EPR data of complex **2a**[8a] are indicative of an unusual intermediate spin state ($S = {}^3/_2$).

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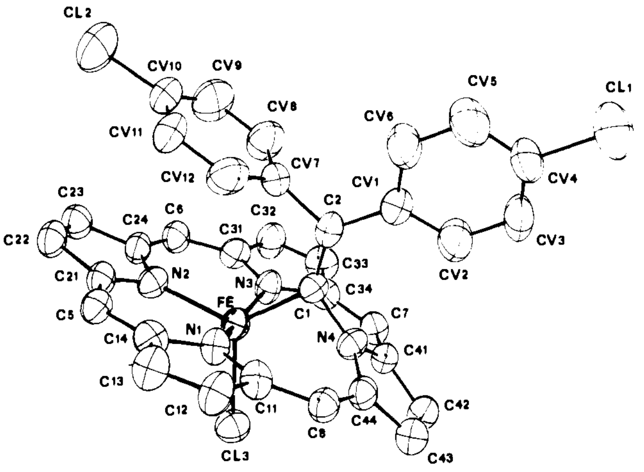

Figure 1. ORTEP drawing of the molecular structure of complex **2b**. The *p*-tolyl groups in meso positions on the porphyrin ligand have been omitted for clarity.

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 **2b**[9] has been prepared by oxidation of the vinylidene complex Fe(TTP)[C=C(p-ClC$_6$H$_4$)$_2$] (**1b**) by CuCl$_2$ 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 five-coordinate. As indicated by the large Fe···N_4 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–Cl$_3$ 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 CHCOOC$_2$H$_5$ carbene[13b] or the NSO$_2$-p-CH$_3$C$_6$H$_4$ 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$_6$H$_6$, CH$_2$Cl$_2$) are identical, ruling out the existence of two different structures in these conditions. Moreover, upon treatment by CF$_3$CO$_2$H, 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)(CHCOOC$_2$H$_5$)[13b] and Co(TPP)(CHCOOC$_2$H$_5$)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] one[4] 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 propose[22] 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 proposed[15] 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 residue[18] 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$_2$O$_2$, or alcohols via two-electron processes.[19]

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(9) Complex **2b**: Elemental analysis corresponds to C$_{62}$H$_{44}$N$_4$FeCl$_3$; visible spectrum (C$_6$H$_6$) λ (ϵ) 428 (5.4×10^4) and 669 (7.8×10^3) nm; $\mu_{eff} = 3.7$ μ_B at 24 °C measured by the Evans method (Evans, D. F. *J. Chem. Soc., Chem. Commun.* **1959**, 2003); EPR in toluene glass at 77 K, $g = 4.4$ and 2.0; mass spectrum, m/e 246 (for ^{35}Cl) corresponding to the C=C(p-ClC$_6$H$_4$)$_2$ moiety; complex **2b** is thermally decomposed at 150 °C (10^{-2} mmHg) leading quantitatively to Fe^{III}(TTP)Cl and RC≡CR (R = p-ClC$_6$H$_4$). **2b** reacts with reducing agents (Na$_2$S$_2$O$_4$) or iron powder to give complex **1b**.

(10) Crystals of Fe^{III}(TTP)[C=C(p-ClC$_6$H$_4$)$_2$]Cl·2C$_2$H$_4$Cl$_2$ (**2b**) belong to the monoclinic system, space group $P2_1/n$ with $a = 20.355$ (5), $b = 12.390$ (3), $c = 23.847$ (5) Å; $\beta = 103.6$ (3)°; $Z = 4$, $d_c = 1.369$ g cm^{-3}. The intensities were measured on a Philips PW 1100 diffractometer by using filtered copper radiation and a flying step scan method. A total of 4305 reflections having $I > 3\sigma(I)$ corrected for absorption were used for structure determination and least-squares refinements. All nonhydrogen atoms including those of the slightly disordered solvent molecules were refined anisotropically. Present values of R_F and R_{wF} are 0.09 and 0.11, respectively.

(11) The short Fe–N_p bond distances (mean value 1.990 Å) and the long axial Fe–Cl bond are both consistent with the presence in **2b** of iron(III) in an intermediate spin state (admixed or pure).[9] (a) Scheidt, W. R.; Reed, C. A., private communication. (b) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, R.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (c) Summerville, D. A.; Cohen, I. A.; Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 2906.

(12) The deviations from the four porphinatonitrogen mean plane are +0.05 Å for N_1 and N_3 and −0.05 Å for N_2 and N_4. 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.

(13) (a) Callot, H. J.; Chevrier, B.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4733. (b) Chevrier, B.; Weiss, R. *Ibid.* **1976**, *98*, 2985. (c) Johnson, A. W.; Ward, D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 720. (d) Johnson, A. W.; Ward, D.; Batten, P.; Hamilton, A. L.; Skelton, G.; Elson, C. M. *J. Chem. Soc.*, Perkin *Trans. 1* **1975**, 2076.

(14) Reaction of **2a** with 2 equiv of CF$_3$CO$_2$H leads quantatively to 2,2-bis(p-chlorophenyl)-*N*-vinyltetraphenylporphyrin characterized by its elemental analysis, mass spectrum (70 eV and 220 °C), M$^+$ 860 for ^{35}Cl and [M − C=C(p-ClC$_6$H$_4$)$_2$]$^+$ 614 for ^{35}Cl; visible spectrum (C$_6$H$_6$) $\lambda(\epsilon)$ 435 (2.2×10^5), 529 (1.2×10^4), 569 (1.5×10^4), 622 (4.1×10^3), and 684 (5×10^3) nm which is very similar to that of *N*-alkyltetraphenylporphyrin: ref 13c. Also: Jackson, A. H. *Porphyrins* **1978**, *1*, Chapter 8.

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(16) (a) Chance, B. *J. Biol. Chem.* **1952**, *194*, 471. (b) Keilin, D.; Nicholls, P. *Biochim. Biophys. Acta* **1958**, *29*, 302. (c) Chance, B. *Arch. Biochem. Biophys.* **1952**, *41*, 416. (d) Roman, R.; Dunford, H. B. *Can. J. Chem.* **1973**, *51*, 588.

(17) Brill, A. S. *Compr. Biochem.* **1966**, *14*, 459.

(18) (a) Yonetani, T.; Schleyer, H.; Ehrenberg, A. *J. Biol. Chem.* **1966**, *241*, 3240. (b) Yonetani, T.; Coulson, A. F. W. *Biochemistry* **1975**, *14*, 2389.

The active oxygen complexes formed upon reaction of ferric hemoproteins of ferriporphyrins with single oxygen donors such as iodosylarenes have been described as $Fe^{V}{=}O$,[8b,15,20] $Fe^{IV}{=}O$ (porphyrin π cation radical),[3,4,15] or $Fe^{IV}R\cdot$ (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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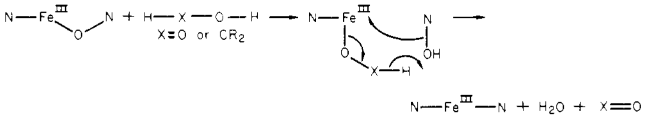
(19) Involving the electrophilic reaction of the oxygen atom of CAT I driven by the regeneration of the Fe–N bond, which can be schematically



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

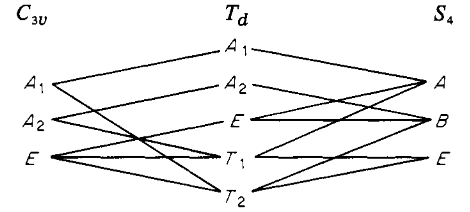
[a] The A atom in each case has the full point symmetry as its site symmetry and C_1 as its interchange symmetry.

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

site symmetry | point symmetry | interchange symmetry



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 $T_d[T_d(X), 4C_{3v}(Y)]$

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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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