ing either by donors (D_Q) or acceptors (A_Q). Which type of quencher is preferred can be rationalized as follows.

(a) The geometry of termolecular excited state interaction (*exterplex*[3] formation if a stable complex is involved) is predictable from simple electrostatics. Thus, a species approximately represented by $D^{\delta+}\cdots A^{\delta-}$ should be quenched from the D side by D_Q, i.e., $D_Q{}^{\delta+}\cdots D^{\delta+}\cdots A^{\delta-}$, or from the A side by A_Q, i.e., $D^{\delta+}\cdots A^{\delta-}\cdots A_Q{}^{\delta-}$. Such a geometry has been suggested[12] by Beens and Weller for the naphthalene–naphthalene–dicyanobenzene *exterplex*.

(b) Our results show a preference for quenching when the interaction occurs with the exciplex component of lower singlet energy (E_s). Thus, the $9CNP^{\delta-}\cdots pBA^{\delta+}$ exciplex clearly prefers A_Q, while the $P^{\delta+}\cdots FN^{\delta-}$ exciplex prefers D_Q. An explanation might derive from the small exciton resonance (ER) binding terms, *c* and *d*, in the equation above. We expect $c > d$ if the molecule of lower E_s acts as D, and $d > c$ if it acts as A. Since the molecule of lower E_s dominates the ER contribution interaction of the quencher with this exciplex partner might lead to more efficient quenching.

Our results suggest preliminary ground rules for exciplex quenching and thus will facilitate the use of the technique for the study of photochemical reactions proceeding through exciplexes (whether emissive or not). The photophysics of the termolecular interaction is under investigation, as are the intriguing predictions for photochemistry that derive from the $D_Q{}^{\delta+}\cdots D^{\delta+}\cdots A^{\delta-}$ and $D^{\delta+}\cdots A^{\delta-}\cdots A_Q{}^{\delta-}$ geometric models.[14]

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Manganese(II) Porphyrins. Synthesis, Structures, and Preference for Five-Coordination

Sir:

Despite research on the incorporation of manganese porphyrins into several reconstituted proteins[1,2] and solution study as models for manganese chlorophylls,[3] manganese(II) porphyrins have not been definitively characterized. Our studies, motivated by the possibility of manganese(II) porphyrins acting as dioxygen carriers, reveal that previously assumed six-coordination is without substantiation. Rather, five-coordination of high-spin Mn(II) prevails. The ramifications of this stereochemical preference on our understanding of the electronically similar heme-iron stereochemistry, and reactions with dioxygen, are discussed.

Reduction of $Mn^{III}Cl(TPP)$[4] with $Cr(acac)_2$ in toluene solution affords purple crystals of the hitherto unknown four-coordinate derivative Mn(TPP)·2(toluene). Unlike its closest analogs, Mn(Pc)[5] and Fe(TPP),[6] which adopt intermediate-spin configurations with in-plane metal ions, magnetic data (μ_{eff} = 6.2 BM) and an X-ray analysis of Mn(TPP) are consistent with a high-spin configuration.

Mn(TPP) provides a good synthetic intermediate for the introduction of axial ligands. Treatment of a toluene solution of Mn(TPP) with ligand L (1-methylimidazole, 2-methylimidazole, or pyridine) gives rise to an intense green solution from which purple crystals can be isolated in high yield. Isosbestic behavior is observed in the visible spectrum throughout the ligation reaction (λ_{max} 525, 569, 605 → 533, 575, 614 nm) and, despite the use of large excesses of ligand L, only *five*-coordinate derivatives have been isolated. All solid samples have magnetic susceptibilities indicative of high-spin d^5 configurations ($\mu_{eff}{}^{25°}$ = 6.2–6.6 BM). The structure of the THF solvate of Mn(TPP)(1-MeIm) has been determined by X-ray analysis.

Diffraction data were collected on a Syntex P$\bar{1}$ diffractometer with Mo Kα radiation. The structures were solved by the heavy-atom method and refined to convergence using anisotropic temperature factors for all heavy atoms. Crystal data and refinement results are as follows: $Mn(N_4C_{44}H_{28})(C_4N_2H_6)\cdot C_4H_8O$, monoclinic; a = 27.405 (7), b = 9.645 (5), c = 17.768 (9) Å; and β = 112.45 (2)°; ρ_{calcd} = 1.258, ρ_{obsd} = 1.27 g/cm³; Z = 4; space group $P2_1/n$; R = 0.052 and R_2 = 0.061;[7] 5276 unique data ($F_o > 3\sigma(F_o)$, $2\theta < 52.9°$); $Mn(N_4C_{44}H_{28})\cdot 2C_7H_8$, triclinic; a = 11.320 (6), b = 11.465 (6), c = 10.487 (6) Å; α = 110.63 (2), β = 103.34 (3), and γ , 107.80 (3)°; ρ_{calcd} = 1.258 g/cm³; Z = 1; space group $P\bar{1}$; R= 0.092 and R_2 = 0.068; 5659 unique data ($F_o > 2\sigma(F_o)$, $2\theta < 63.7°$).

The structure of Mn(TPP) provides one answer to an interesting question of porphyrin stereochemistry, namely, whether independent of coordination number, a large metal ion takes an out-of-plane position from the porphinato nitrogen atoms. With one molecule per cell,[8] the point group symmetry (real or statistically effective) required of the Mn(TPP) molecule is C_i. Refinement with the Mn(II) ion positioned at the center of symmetry (center of the porphyrin molecule) leads to a Mn–N bond distance of 2.082 Å, possibly consistent with a high-spin ion.[9] However, the anisotropic thermal parameter of the Mn(II) ion, perpendicular to the mean porphinato plane, is unrealistically large (root mean square displacement 0.351 Å). An alternate refinement in which the Mn(II) ion was allowed to take an out-of-plane position, while retaining a statistical center of symmetry, leads to a slightly less unrealistic thermal parameter (root mean square 0.28, Figure 1) despite an identical R factor. Either alternative suggests that the Mn atom is out-of-plane in accord with theoretical calculations[10]

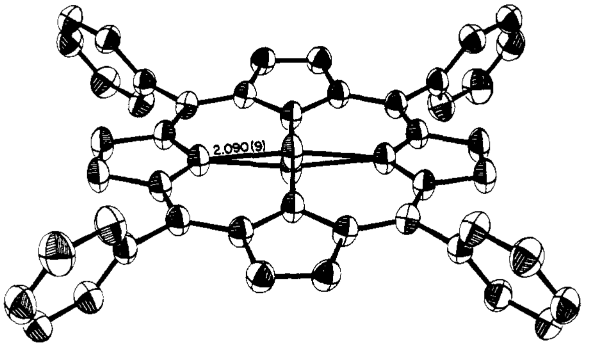

Figure 1. Model in perspective of the Mn(TPP) molecule with the manganese(II) ion allowed to take an out-of-plane position. Atoms are represented by their vibrational ellipsoids, contoured to enclose 50% of the electron density.

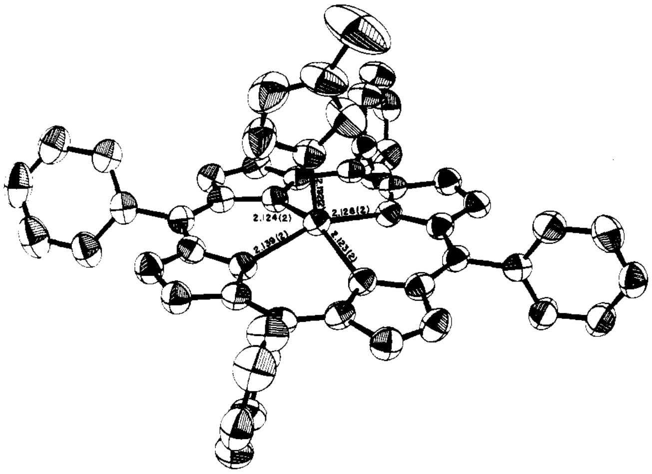

Figure 2. Model in perspective of the Mn(TPP)(1-MeIm) molecule. Atoms are represented as in Figure 1.

which predict that a Mn(II) ion must be intermediate spin in order to be in-plane. The Mn-N bond distance of 2.090 Å corresponds to a displacement of 0.19 Å out-of-plane (this is a minimum estimate); the Ct···N distance remains constant at 2.082 Å. The out-of-plane displacement may be either a static or dynamic process; the large radius of the central hole suggests that the dynamic process is physically reasonable. Low-temperature structural studies are planned.

The average Mn-N(porphyrin) bond distance of 2.128 Å in five-coordinate Mn(TPP)(1-MeIm) (Figure 2) again illustrates the large size of the ion. The Mn(II) ion is displaced 0.56 Å out of the mean porphyrin plane. The central hole of the porphyrin has expanded to accommodate the Mn(II) ion; Ct···N is 2.065 Å. The molecular stereochemistry is readily interpreted in terms of the high-spin d^5 configuration. The population of the $d_{x^2-y^2}$ orbital (whose lobes are directed toward the porphinato-nitrogen atoms), by an essentially antibonding electron, causes a large out-of-plane displacement of the Mn(II) ion, thereby thwarting strong bonding interactions with a further axial ligand in the sixth coordination site. We suspect that six-coordination can occur in isolable complexes only if accompanied by a change to a low-spin configuration where $d_{x^2-y^2}$ is empty. So far, we have been unable to find ligands to effect this change despite variation of TPP to octaethylporphyrin and ligand variation among imidazoles, pyridines, phosphines, THF, and O_2.[11] In contrast, phthalocyanine, a possibly stronger field ligand with a smaller "central hole" for the metal ion,[13] is reported to give rise to the low-spin derivative Mn(Pc)(py)$_2$ in solution.[14] It has not, however, been isolated.[15]

The bond parameters of the MnN_5 coordination group are all slightly larger than those of the FeN_5 coordination group of the related high-spin Fe(TPP)(2-MeIm) complex,[16] wherein Fe-N(porphyrin) is 2.086 Å, Ct···N is 2.044 Å, and the iron is displaced 0.55 Å out of the mean porphinato plane. The axial bond distances also show the same trend with Fe-N = 2.161 Å and Mn-N = 2.192 Å. Our results corroborate the heme-iron stereochemical description recently established by Hoard and collaborators,[6,17] and theoretically argued by Gouterman et al.[18] High-spin Fe(II), Fe(III), and now Mn(II) porphyrins display five-coordination with out-of-plane metal ion displacements of 0.42-0.56 Å toward the axial ligand. Moreover, the close structural similarity of the deoxyhemoglobin model, Fe(TPP)(2-MeIm), to the presert model for manganese hemoglobin (MnHb) strongly supports the expectation[19] that the quaternary structures of Hb and MnHb are identical.

MnHb does not carry dioxygen; rather, irreversible oxidation to Mn^{III}Hb occurs.[1] Our observatiors lead to an explanation of the former fact but not the latter. Predictably, solutions of four-coordinate Mn(TPP) are oxidized rapidly and irreversibly upon exposure to air or dioxygen to a Mn(III) product (distinctively split Soret peak). On the other hand, solutions of the five-coordinate complexes Mn(TPP)L or Mn($\alpha,\alpha,\alpha,\alpha$-TpivPP)L derived from "picket fence" porphyrin[20] are essentially unaffected by dioxygen if small molar excesses of axial ligand are present. Slow irreversible oxidation to Mn(III) products does eventually occur, however, over several hours. The lack of dioxygen-carrying ability can be understood in terms of our previously established preference for five-coordination. Since dioxygen coordination in the hypothetical Mn(O_2)(TPP)L (or MnHbO_2) is apparently incapable of causing a change to low-spin, a *six*-coordinate dioxygen adduct does not form. Largely reversible oxygenation of a toluene-THF solution of Mn(TPP) at −90° apparently produces the *five*-coordinate dioxygen complex Mn(O_2)(TPP) whose definitive characterization we are seeking.

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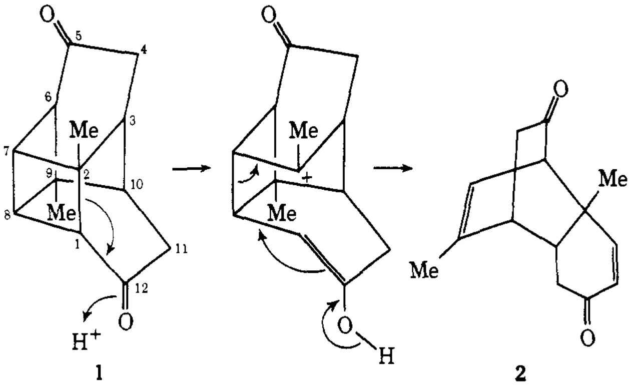
Stereospecific Acid-Catalyzed Rearrangement of 1,6-Dimethylpentacyclo[6.4.0.0^{2,7}.0^{3,10}.0^{6,9}]dodecane-5,12-dione to a Bisnordiadamantane

Sir:

On treatment with trifluoroacetic acid at room temperature, pentacyclo[6.4.0.0^{2,7}.0^{3,10}.0^{6,9}]dodecane-5,12-diones having a methyl group at C-2 (**1**), synthesized photochemically from Diels–Alder dimers (**2**) of cyclohexa-2,4-dienones, reverted easily to **2** in high yield.[1] Stabilization of a carbonium ion at C-2 by a methyl group was assumed to be the most important requirement for this acid-catalyzed reversion.[1b]

A cage compound, with a methyl group at C-1, on acid treatment would be expected to release most of the strain of the bicyclo[2.2.0]hexane system in a different way as shown here by the stereospecific rearrangement of the representative **3**.



1 **2**

When **3** was heated under reflux in trifluoroacetic acid for 15 min, or in benzene with *p*-TsOH for 45 min, the isomeric rearrangement product **4** was isolated in almost quantitative yield: mp 182–184°, from *n*-hexane; ν^{Nujol} 1735 cm^{-1}; *m/e* 272 (M$^+$); ^{1}H nmr $\delta^{\mathrm{CDCl_3}}$ 0.84 (s, 6 H), 0.96 (s, 6 H), 0.96 (s, 6 H), 1.03 (s, 6 H), 2.38 (m, 4 H), 2.48 (m, 2 H); ^{13}C nmr $\delta^{\mathrm{CDCl_3}}$ 11.6 (CH$_3$), 20.6 (CH$_3$), 26.8 (CH$_3$), 48.4 (C), 52.2 (CH), 53.8 (CH), 57.2 (C), 57.5 (CH).

Protonation of one of the carbonyl groups in **3** causes the formation of the methyl-stabilized carbonium cation at C-1 through rearrangement of either bond a or b, followed by another set of *twofold Wagner–Meerwein rearrangements* to yield a less strained cage compound, such as **4**, **5**, or **6**. A few precedents of such rearrangements have been reported in simpler cases, propellanones[2] and spiranone.[3] Both **4** and **5** have a twofold axis of symmetry whereas **6** has not. Since ^{1}H and ^{13}C NMR spectra clearly indicate that the product is symmetric, **6** is excluded. Although it is impossible to distinguish between **4** and **5** by the usual spectral data, there is a marked difference in their dipole moments: estimated value for **4** ca. 4.0 D; and for **5** ca. 0.0 D. The observed value (ca. 4.2 D) shows that **4** is the correct structure, a conslusion which is confirmed by Roentgen-ray analysis.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with a = 6.818 (4) Å, b = 12.586 (5) Å, c = 17.966 (8) Å, and β = 106.8 (1)°. There is one molecule per asymmetric unit corresponding to a calculated crystal density of 1.22 g/cm^3. The structure was solved by the symbolic addition procedure for centrosymmetric crystals[4] and refined by full-matrix least-squares methods[5] to an R factor of 5.8%. The stereodrawing[6] in Figure 1 which was constructed with the experimentally determined atomic coordinates displays the results of the X-ray analysis. Within experimental error, the molecule has twofold rotation symmetry.[7] So far cedrone[8] seems to be the only other representative of the interesting bisnordiadamantane type.

The most important reason for the favored rearrangement of bond a must lie in the stability difference between the rearranged cations **3a** and **3b** both of which arise by conversion of the strained four, six, six-membered ring system in **3** (thick line) to the more stable five,five,six system with release of strain energy. Inspection of models clearly indicates that the six-membered cationic structures, **3a** and **3b** (shaded parts), are quite different, though the strain in the remainder of the molecules may be the same. The six-membered ring in **3a** is present in a normal chair conforma-

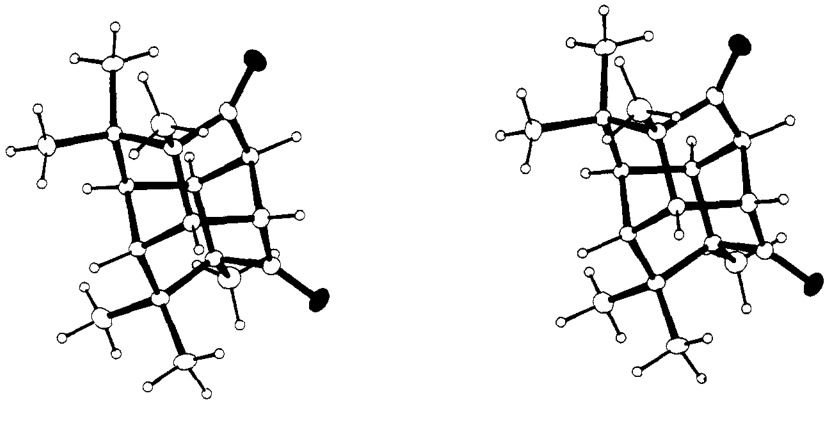


Figure 1. Stereodrawing of compound **4** executed with the experimentally determined coordinates from a crystal structure analysis. The shaded ellipses represent oxygen atoms.