under a PES peak is proportional to the abundance of the rotamer.[11]

While the actual per cent compositions in Table I differ from those estimated by vibrational spectroscopy[12] for $(CH_3)_4P_2$,[2a,d] $(CF_3)_4P_2$,[2b] and $(CH_3)_4As_2$,[3b] the qualitative trends in the PES data substantiate the generalizations that have been made for A_2X_4 species;[13] viz., the trans conformer is favored by (a) increasing the A–A bond distance and (b) increasing the electronegativity of X. The PES results, however, are not in accord with the electron diffraction study of $(CH_3)_4P_2$ which indicated that this molecule exists exclusively in the trans conformation.[2c] Despite the steric bulk of the C_6F_5 moiety, the fact that no gauche rotamer is detectable in $(CF_3)_4As_2$ (by PES or vibrational spectroscopy[3c]) contrasts sharply with the claim[3a] that $(C_6F_5)_4As_2$ can be separated into gauche and trans rotamers.

(11) Such an assumption may not be generally valid since photo-ionization cross sections are dependent upon several factors such as the symmetry and orbital character of the MO from which the electron is removed and the relative energies of the light source and the MO in question. See, for example, L. L. Lohr, Jr., and M. B. Robin, *J. Amer. Chem. Soc.*, **92**, 7241 (1970); W. Thiel, Ph.D. Dissertation, Philipps Universität, Marburg/Lahn, West Germany, 1973. However, in the case of the ionization of the lone pair MO's of the trans and gauche rotamers of hydrazine-like molecules, this assumption is reasonable because the orbitals are close in energy and similar in character.

(12) This approach is based on the assumption that Raman peak intensities are proportional to the abundances of the rotamers. This assumption is clearly questionable since the dipole moments of the two rotamers must differ and their derivatives should differ likewise.

(13) For a review see J. R. Durig, B. M. Gimarc, and J. D. Odom in "Vibrational Spectra and Structure," Vol. 2, J. R. Durig, Ed., Marcel Dekker, New York, N. Y., 1973.

A. H. Cowley,* M. J. S. Dewar*
D. W. Goodman, M. C. Padolina

*Department of Chemistry, University of Texas at Austin
Austin, Texas 78712*

Coordination Geometries of High-Spin Manganese(III) Porphyrins and Their Synthetic Intermediates

Sir:

This report contains recent results which help clarify previous ambiguities about some aspects of Mn(III) coordination chemistry.[1] These results clearly demonstrate the expected formation of distorted octahedral complexes of high-spin Mn(III)—a result contrary to some published structural work.[2] This distortion, which frequently manifests itself in the form of a tetragonal elongation, is probably responsible for the ready incorporation of Mn(III) into porphyrins.[3,4] The results reported herein also tend to contradict to some extent those which report high-spin octahedral manganese(III) porphyrins containing a very tightly co-ordinated axial neutral Lewis base which cannot be removed even under rather severe conditions.[5]

A series of manganese(III) porphyrins having general formulas, Mn(TPP)(X) and Mn(TPP)(X)(B), where TPP is the $\alpha,\beta,\gamma,\delta$-tetraphenylporphinato dianion, X is a mononegative anionic ligand such as N_3^-, NCS^-, or Cl^-, and B is a neutral Lewis base such as pyridine or methanol, have been synthesized from the corresponding acetylacetonate (acac) complexes, $Mn(acac)_2(X)$ or $Mn(acac)_2(X)(B)$.[4] The results of single-crystal X-ray structural investigations for $Mn(TPP)(N_3)(CH_3OH) \cdot CH_3OH$ and its synthetic intermediate, $Mn(acac)_2(N_3)$, as well as $Mn(acac)_2(NCS)$ and γ-$Mn(acac)_3$, demonstrate several interesting facets of Mn(III) coordination chemistry and their effect in the biologically important manganese porphyrins.[6]

Three-dimensional diffraction data on all compounds were collected on a computer-controlled four-circle Syntex P_I autodiffractometer using Nb-filtered Mo $K\bar{\alpha}$ radiation and ω or θ–2θ scans. Except for the structure of $Mn(acac)_2(NCS)$ which required the use of "direct" methods, all structures were solved using the heavy-atom technique. The structural parameters for each compound have been refined to convergence in cycles of unit-weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for all non-hydrogen atoms.

Crystal data and refinement results are as follows. $Mn(O_2C_5H_7)_2(N_3)$ monoclinic; $a = 11.527$ (4), $b = 10.005$ (4), $c = 11.263$ (3) Å; $\beta = 94.86$ (3)°; $D_{calcd} = 1.514$, $D_{measd} = 1.499$ g cm^{-3}; $Z = 4$ (molecular units); space group $C_{2/c}$; $R = 0.042$ for 1908 independent reflections having $2\theta_{MoK\bar{\alpha}} < 63.7°$ and $I > \sigma(I)$; data-to-parameter ratio = 17.0 for ten anisotropic non-hydrogen atoms and seven isotropic hydrogen atoms. $Mn(O_2C_5H_7)_2(NCS)$ orthorhombic; $a = 13.422$ (2), $b = 14.519$ (3), $c = 13.763$ (3) Å; $D_{calcd} = 1.541$, $D_{measd} = 1.540$ g cm^{-3}; $Z = 8$ (molecular units); space group P_{bca}; $R = 0.057$ for 1917 independent reflections having $2\theta_{MoK\bar{\alpha}} < 55°$ and $I > 2\sigma(I)$; data-to-parameter ratio = 11.8 for 18 anisotropic nonhydrogen atoms. γ-$Mn(O_2C_5H_7)_3$ monoclinic; $a = 7.786$ (1), $b = 27.975$ (4), $c = 8.020$ (1) Å; $\beta = 100.34$ (1)°; $D_{calcd} = 1.361$, $D_{measd} = 1.366$ g cm^{-3}; $Z = 4$; space group $P_{2_1/n}$; $R = 0.062$ for 1696 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > \sigma(I)$; data-to-parameter ratio = 8.5 for 22 anisotropic nonhydrogen atoms (refinement is continuing with a data set twice as large). $Mn(N_4C_{44}H_{28})(N_3)(CH_3OH) \cdot CH_3OH$ monoclinic; $a = 19.095$ (2), $b = 9.790$ (2), $c = 46.927$ (6) Å; $\beta = 106.35$ (1)°; $D_{calcd} = 1.221$, $D_{measd} = 1.282$ g cm^{-3}; $Z = 8$; space group $C_{2/c}$; $R = 0.096$ for 3569 independent reflections having $2\theta_{MoK\bar{\alpha}} < 45.8°$ and $I > 2\sigma(I)$; data-to-parameter ratio = 7.1 for 56 anisotropic nonhydrogen atoms (refinement is continuing with a data set twice as large).

The crystallographic studies for $Mn(acac)_2N_3$ and $Mn(acac)_2(NCS)$ have shown that, in both compounds, the mononegative anionic ligand, X, bridges adjacent Mn(III) atoms in the three-dimensional lattice to form polymeric chains of six-coordinate (rather than five-coordinate) Mn(III) polyhedra. Both compounds exhibit a large tetragonal elongation of the octahedral

(1) See, for instance, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1972, p 851.

(2) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, **17**, 705 (1964).

(3) R. Khosropour and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).

(4) B. R. Stults, V. W. Day, E. L. Tasset, and R. S. Marianelli, *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).

(5) L. J. Boucher, *J. Amer. Chem. Soc.*, **90**, 6640 (1968). See also ref 6.

(6) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972), and references cited therein.
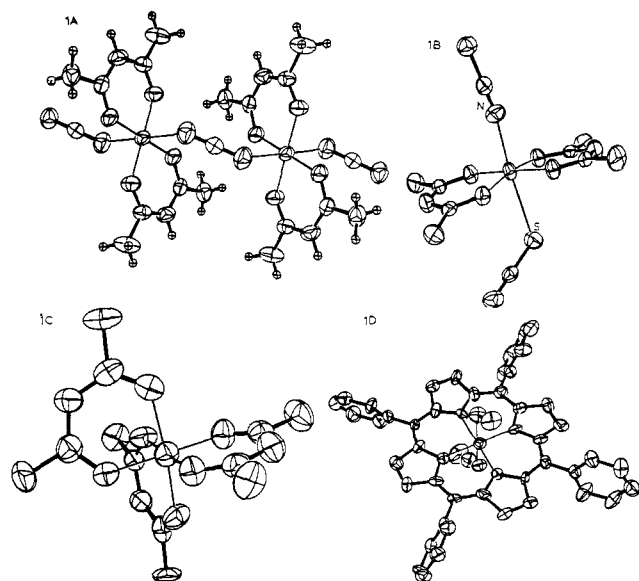
Figure 1. ORTEP drawings showing: for Mn(acac)$_2$(N$_3$), two Mn(acac)$_2$(N$_3$) units plus an additional (coordinated) azide ligand, 1A; for Mn(acac)$_2$(NCS), a Mn(acac)$_2$(NCS) unit plus an additional (coordinated) thiocyanate ligand, 1B; a complete γ-Mn(acac)$_3$ molecule, 1C; and a complete Mn(TPP)(N$_3$)(CH$_3$OH) molecule, 1D. All nonhydrogen atoms are represented by ellipsoids which reflect the refined anisotropic thermal parameters. Hydrogen atoms are shown only for Mn(acac)$_2$(N$_3$) and are represented by arbitrarily small spheres in no way representative of their true thermal motion.

Figure 2. ORTEP drawings of the coordination polyhedra for Mn(acac)$_2$(N$_3$), 2A; Mn(acac)$_2$(NCS), 2B; γ-Mn(acac)$_3$, 2C; and Mn(TPP) (N$_3$)(CH$_3$OH)·CH$_3$OH, 2D. All nonhydrogen atoms are represented by ellipsoids which reflect the refined anisotropic thermal parameters.

Mn(III) coordination polyhedron with four short, 1.910 (4, 3, 7) Å,[7] Mn–O bonds to each atom in the quasisquare array of acetylacetonate oxygen atoms and two long (by at least 0.20 Å) trans Mn–X bonds to the ends of the bridging X ligand.

These results, combined with Fackler's recent disclosure[8] that the compound reported by Morosin and Brathovde[2] in 1964 to gave an undistorted octahedral coordination polyhedron was most likely Co(acac)$_3$ and not Mn(acac)$_3$, led us to reexamine the Mn(acac)$_3$ problem as well. In addition to the β-monoclinic form of Mn(acac)$_3$ that is virtually isomorphous with the β-Co-(acac)$_3$ reported by Morosin and Brathovde and which has been reexamined by Fackler, we have isolated a second monoclinic form of Mn(acac)$_3$. This form, γ-Mn(acac)$_3$, possesses a tetragonal elongation of the octahedral coordination polyhedron, having four short (1.929 (6, 6, 10) Å) and two long (2.116 (6, 6, 6) Å) Mn–O bonds.

A similarly distorted octahedral geometry is observed for Mn(TPP)(N$_3$)(CH$_3$OH)·CH$_3$OH. The four Mn–N bonds involving the porphyrin ligand average 2.031 (7, 10, 15) Å while the azide Mn–N and methanol Mn–O bond lengths are 2.176 (9) and 2.329 (7) Å, respectively. Unlike the porphine skeletons of many other metalloporphyrins, the 24-atom (excluding hydrogen atoms) porphine skeleton in Mn(TPP)(N$_3$)-(CH$_3$OH)·CH$_3$OH is nearly planar (maximum deviation of any atom from the least-squares mean plane is 0.057

Å) with the Mn atom displaced from it by 0.086 Å toward the coordinated azide ligand. A crystalline product having chemical and physical properties consistent with a formulation of Mn(TPP)(N$_3$) can be obtained by recrystallizing Mn(TPP)(N$_3$)(CH$_3$OH)·C-H$_3$OH from a benzene–heptane mixture. The three-dimensional crystal structure of this compound is currently under investigation; a bridged structure similar to that of Mn(acac)$_2$(N$_3$) or a five-coordinate species similar to that of Mn(TPP)(Cl)[9,10] is anticipated. Figure 1 shows complete ORTEP drawings for all four compounds; the structural similarities of all four-coordination polyhedra can be seen in Figure 2.

These structures dramatically demonstrate the operation of electronic effects in distorting the coordination polyhedra of high-spin Mn(III) complexes. It is this ability of high-spin Mn(III) to distort its coordination sphere which permits its incorporation into the plane of the porphine skeleton, in sharp contrast with high-spin Fe(II) and Fe(III) which must go to the low-spin state before fitting into the size-restricting porphine skeleton.

The results of these structural studies and others[8,11-14] indicate a definite preference (at least in the solid state) for a coordination number of six rather than five for

(7) The first number in parentheses is the rms value of the estimated standard deviation for a single datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.

(8) J. P. Fackler, Jr., and A. Avdeef, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, No. INOR 64.
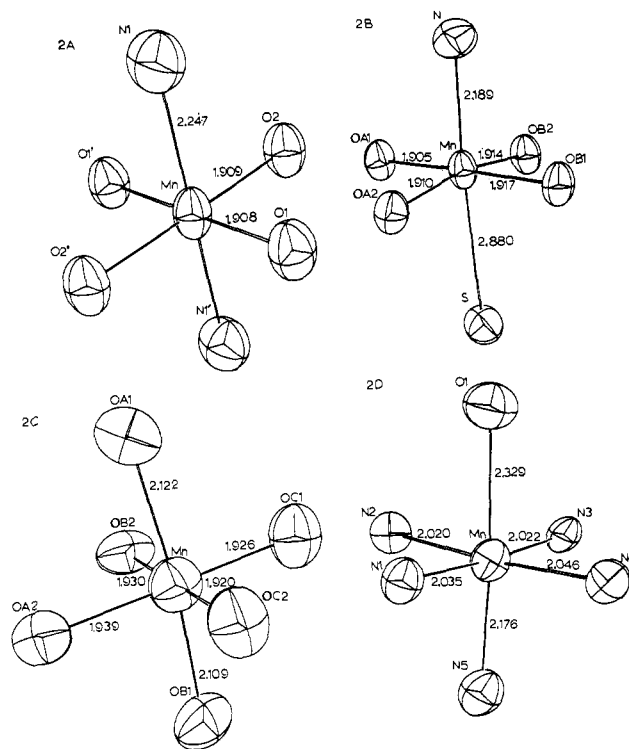
(9) B. M. Chen and A. Tulinsky, unpublished data; B. M. Chen, Ph.D. Thesis, Michigan State University, 1970. See also ref 6.

(10) J. L. Hoard, private communication.

(11) M. Bartlett and G. J. Palenik, *Chem. Commun.*, 416 (1970).

(12) J. P. Fackler, Jr., A. Avdeef, and J. Costamagna, Proceedings of the International Conference on Coordination Chemistry, XIV, Toronto, Canada, June 1972.

(13) K. Knox, Abstracts of the 6th International Congress of the International Union of Crystallography, Rome, 1963; *Acta Crystallogr. (Suppl.)*, 16, A45(1963).

(14) P. C. Healey and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972).

discrete high-spin Mn(III) complexes and for a pronounced tetragonal distortion of the coordination polyhedron.

In the case of manganese(III) porphyrins, the structural data for two crystalline forms of Mn(TPP)Cl[9, 10] and the results reported herein lead to the expectation of stable six-coordinate complexes when high-spin manganese(III) porphyrins of the general formula Mn(Por)(X) are in the presence of, or crystallized from, strongly coordinating solvents and five-coordinate species when in the presence of, or crystallized from, weakly coordinating solvents. In the latter case the coordination polyhedron would be characterized by having the Mn atom displaced from the porphine skeleton toward the anionic X ligand and a Mn–X bond of "normal" length. In the former case the distinguishing characteristics would be "long" bonds from the axial ligands to a Mn atom which might be more nearly in the porphine plane.

V. W. Day,* B. R. Stults, E. L. Tasset
R. O. Day, R. S. Marianelli*

*Department of Chemistry, University of Nebraska–Lincoln
Lincoln, Nebraska 68508*

Trapping of the Carbene Intermediates in the Photolysis of Triptycenes

Sir:

The photochemical isomerization of triptycene (tribenzobarrelene) (**1**)[1] is unique among barrelene derivatives[2, 3] in that the single product (**2**) which is neither the expected semibullvalene (**3**) nor a cyclooctatetraene derivative is formed smoothly in inert as well as in photosensitizing solvents. On the assumption that the pathway for triptycene photoisomerization should not be drastically different from that elucidated for barrelene,[2] the photoproduct **2** was considered as being formed by a 1,5-sigmatropic rearrangement of **3** which might be initially formed by way of the di-π-methane rearrangement of **1** (path a in Scheme I).[1, 4]

We have been advocating for a couple of years the carbene mechanism for the photolytic rearrangement of **1** to **2** (path b in Scheme I)[5] and wish to report here on

two trapping experiments of the carbene intermediates **4** and **4a**.

Irradiation of a 0.003 M solution of **1** in methanol under nitrogen for 2 hr with a Vycor filtered Ushio UM-452 500-W high-pressure mercury source in an immersion apparatus resulted in 85% consumption of the starting material. The photoproduct isolated by tlc on silica gel was not the reported **2**[1] but was identified as 9-(2-methoxymethylphenyl)fluorene (**5**): colorless needles; mp 120–121°; in 75% isolated yield based on the unrecovered **1**; nmr (CDCl$_3$) δ 3.51 (s, CH$_3$O), 4.84 (s, OCH$_2$), 5.46 (s, C$_9$–H), 6.39 (dd, $J = 8.1, 2.0$ Hz, C$_{6'}$–H), 7.1–7.5 (m, 9 aromatic H's), and 7.6–7.9 (m, 2 aromatic H's).[6–8] An authentic sample for comparison was prepared by methanolysis of 9-(2-iodomethylphenyl)fluorene.[5b] A preliminary result on the quantum efficiency ($\phi = 0.3$) of formation of **5** was not different from that of **2** in inert solvents.[1] Photoproduct **2** is also not stable in methanol under irradiation.[9] However, the main product is 8,12b-dihydrobenz[a]aceanthrylene: colorless prisms, mp 139–140°,[10] in 57% yield.[11]

When a solution of 1-acetyltriptycene (**6**) was irradiated similarly in methanol, no trace of the normal isomerization products, **7**, was detected as evidenced by lack of the characteristic uv absorption at 350 nm due to the chromophore of **2**[1,5] in the crude reaction mixture. The photoproduct, mp 115–116°,[6] was separated in 68% yield from the starting material by tlc on silica gel and has been identified as **8** on the basis of spectral analysis. The mass spectrum shows a molecular ion at m/e 328 (M) with other prominent peaks at 296 (M – CH$_4$O), 268 (M – C$_2$H$_4$O$_2$), 253 (M – C$_3$H$_7$O$_2$; base peak), and 241 (M – C$_4$H$_7$O$_2$). The infrared spectrum (KBr disks) indicates the presence of an aliphatic ester group at 1738 and 1210 cm^{-1}. The uv absorptions λ_{max}, nm (log ϵ) in methanol are 255 (3.81), 267 (4.15), 292 (3.57), and 303 (3.81). The nmr spectrum is essentially first order and shows the presence of two conformers in a ratio of 2.2:1. The dominant conformer shows a three-proton doublet at δ 1.73 ($J = 7.1$ Hz), an OCH$_3$ singlet at 3.77, a methine quartet at 4.55 ($J = 7.1$ Hz), a C$_9$–H singlet at 5.46, a characteristic double doublet due to C$_{6'}$–H at 6.35, and aromatic

(1) T. D. Walsh, *J. Amer. Chem. Soc.*, **91**, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, *ibid.*, **91**, 516 (1969).

(2) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

(3) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191, 6096 (1968); P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968); E. Ciganek, *ibid.*, **88**, 2882 (1966); R. S. H. Liu, *ibid.*, **90**, 215 (1968).

(4) The molecular frameworks of these compounds require that the 1,5-sigmatropic rearrangement of **3** to **2** should be the suprafacial shift with inversion of configuration at the migrating center. The process is symmetry-forbidden in the ground state, and reexcitation of **3** is necessary for path a to be an energetically favorable reaction. Since the photoisomerization is rather efficient,[1] a two-photon process cannot be highly likely.

(5) The circumstantial evidences in support of the carbene mechanism found in these laboratories are (a) lack of interconversion of the atropisomeric 1,6-bis(1-cyano-1-methylethyl)triptycenes under irradiation (rotation of the pivot bonds extending from the bridgehead to the substituents in the intermediates for the di-π-methane rearrangement followed by decay to the starting material would result in mutual isomerization of the meso and *dl* isomers of the recovered triptycenes: H. Iwamura, The 4th IUPAC Symposium on Photochemistry, Baden-Baden, Germany, July 16–22, 1972, abstracts of contributed papers, p 104; *J. Chem. Soc., Chem. Commun.*, 232 (1973)), (b) formation of **2** from **4** generated independently from the corresponding diazo compound (H. Iwamura, *Chemistry Lett.*, 5 (1974)), and (c) unique product distribution of a series of substituted triptycenes (to be published elsewhere).

(6) All new compounds have satisfactory analytical data.

(7) The nmr signals are relatively broad because the averaging of the chemical shifts between the conformers due to the restricted rotation around the aryl–C$_9$ bond is incomplete at 34° under 60 MHz. In a probe heated at 50° the signals are reasonably sharp. A precedent can be found in 9-(*o*-tolyl)fluorene.[8]

(8) T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969).

(9) We are grateful to the referees for pointing out this possibility. Except for the quantum efficiency data, an operational test to rule out the remote possibility of **3** fragmenting under reaction conditions to give carbene **4** could not be designed.

(10) N. Campbell and A. Marks, *J. Chem. Soc.*, 2941 (1951).

(11) Small amount of intractable oil containing the methoxyl group as revealed by its nmr is also obtained.