Acknowledgment. We thank Dr. Sueo Nishi for his advice on the GC/mass spectra, Professor Shigeru Oae for his encouragement, and Professor Manfred K. Eberhardt for his helpful suggestions concerning our manuscript.

Registry No. 1, 11084-15-4; **3**, 72437-42-4; benzene, 71-43-2; toluene, 108-88-3.

Structural Characterization of a Complex of Manganese(V): Nitrido[tetrakis(*p*-methoxyphenyl)porphinato]manganese(V)

Craig L. Hill* and Frederick J. Hollander

Department of Chemistry, University of California
Berkeley, California 94720

Received August 30, 1982

The current intense interest in high-valent manganese porphyrins derives from the ability of these complexes to oxidize water both thermally[1] and photochemically[2] and to oxidize hydrocarbons under very mild conditions.[3,4] Although two Mn(IV) porphyrin complexes, the dimeric complex $[N_3Mn^{IV}TPP]_2O$[5,6] and the monomeric complex $(CH_3O)_2Mn^{IV}TPP$,[7] were recently structurally characterized by X-ray crystallography, no Mn(V) porphyrin complexes have been structurally characterized.[8] Indeed the only complexes with Mn in the 5+ oxidation state for which there exists compelling evidence are those with oxide and halide ligands.[9,10] We report here the principal structural properties of the complex nitrido[tetrakis(*p*-methoxyphenyl)porphinato]manganese(V) ($NMn^{V}T$*p*MPP,[5] **1**) and selected physical and chemical properties of **1** and the analogous TPP and T*p*TP complexes.[5]

In the course of our research on catalytic hydrocarbon functionalization by Mn porphyrin complexes,[3,4a,6] we examined the effect of introducing ammonia to the $XMn^{III}TPP$–iodosylbenzene system in order in assess the possibility of activating both ammonia and hydrocarbon to form carbon–nitrogen bonds. When $XMn^{III}TPP$, X = Cl, Br, and OAc, and iodosylbenzene react with a large excess of ammonia in dichloromethane solution, the crude nitride complex $NMn^{V}TPP$ precipitates from solution in yields as high as 96% based on $XMn^{III}TPP$. In a typical preparation 0.25 g (3.4×10^{-4} mol) of $AcOMn^{III}TPP$ is added to 25 mL of degassed CH_2Cl_2 containing 2 mL of NH_3 in a Schlenk flask under a stream of argon. To this green solution are added 1.0 g (4.5×10^{-3} mol) of iodosylbenzene in 0.05-g portions and 3 mL of NH_3 dropwise over a period of 15 min. After an additional 30 min of stirring, the minimally soluble crude $NMn^{V}TPP$ is collected and recrystallized from toluene–hexane.[11] The reaction of ammonia with the isolated high-valent MnTPP–iodosylbenzene complexes[4] also produces the nitride complex in ca. 70% yield, but the reactions of ammonia with the other high-valent Mn porphyrins, $[YMn^{IV}TPP]_2O$ (Y = N_3 or OCN, or $(CH_3O)_2Mn^{IV}TPP$), lead only to the usual thermally stable $[Mn^{III}TPP]^+$ decomposition products. Recently Buchler and co-workers prepared nitrido manganese(V) porphyrin complexes by another synthetic method.[10]

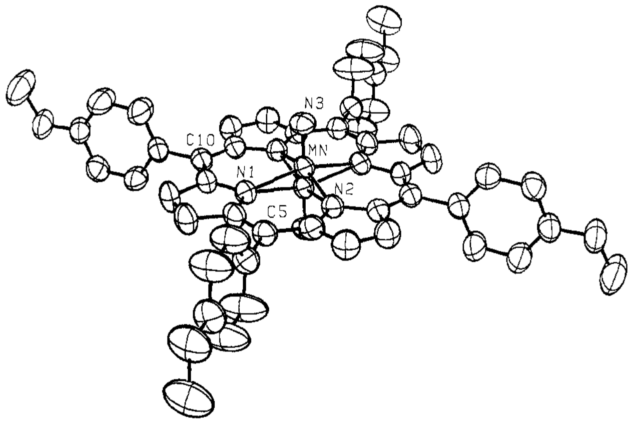

Figure 1. ORTEP diagram of **1** displaying 50% probability ellipsoids. The Mn≡N moiety is disordered 50–50 above and below the N_4 plane.

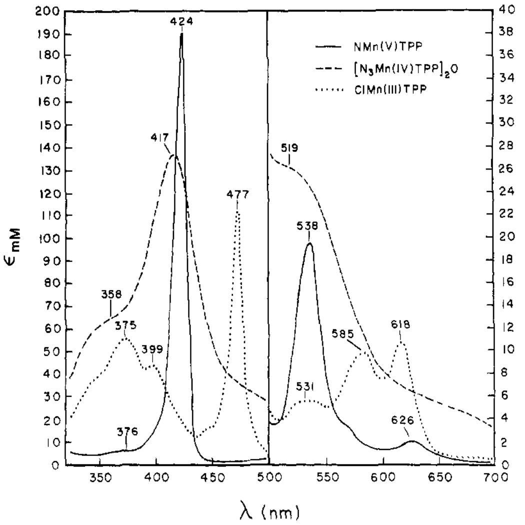

Figure 2. Electronic spectra of $NMn^{V}TPP$, $[N_3Mn^{IV}TPP]_2O$, and $ClMn^{III}TPP$. The spectrum of $NMn^{V}TPP$ from λ 320–500 nm is half scale. All spectra are recorded as ca. 1 mM solutions in chlorobenzene at 25 °C.

The tetrakis(*p*-methoxyphenyl)porphyrin ligand, T*p*MPP, unlike the TPP, T*m*TP, and T*p*TP[5] ligands, facilitated the growth of diffraction-quality single crystals of the manganese(V) porphyrin nitride complex. The lustrous red prisms of a chlorobenzene solvate of **1** submitted to structural analysis by X-ray crystallography were grown by allowing hexane to diffuse into a chlorobenzene solution of **1** at 25 °C over a period of 3 days. The unit cell and refinement results are as follows: $NMn^{V}(TpMPP)\cdot nC_6H_5Cl$, $n \leq 1$, monoclinic with space group $C2/c$, $Z = 4$, $a = 30.5128$ (22) Å, $b = 9.5508$ (10) Å, $c = 15.2593$ (14) Å, $V = 4442.1$ (12) Å^3, M_r for $n = 1$ is 914.35 amu, unique reflections used in least squares = 2117 with $F_0^2 > 3\sigma(F_0^2)$, $R = 4.19\%$.[12] Disordered chlorobenzene molecules occupy holes

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[5] Abbreviations: TPP, T*m*TP, T*p*TP, T*p*MPP designate the tetraphenyl, tetra-*m*-tolyl, tetra-*p*-tolyl, and the tetrakis(*p*-methoxyphenyl) porphyrin dianion ligands, respectively.

[6] Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964–3972.

[7] The complex $(CH_3O)_2Mn^{IV}TPP$ has been prepared by three synthetic methods and characterized by X-ray crystallography and other physical methods. Cf.: Camenzind, M. J.; Hollander, F. J.; Hill C. L. *Inorg. Chem.*, in press.

[8] Buchler, Scheidt, and their co-workers recently completed the X-ray structure of a porphodimethenenitridomanganese(V) complex: Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.*, in press.

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[10] Buchler and co-workers recently prepared nitrido manganese(V) porphyrin complexes by oxidizing Mn(III) porphyrin complexes with hypochlorite in the presence of ammonia: Buchler, J. W.; et al. *Z. Naturforsch., B*, in press. Their nitrido complexes have properties similar to the properties of ours.

[11] The complexes $NMn^{V}TPP$ and $NMn^{V}TpTP$ crystallize from toluene–hexane or benzene–hexane as solvate-free crystals, and **1** crystallizes from *N*-methylpyrrolidinone (NMP)–water or chlorobenzene–hexane as NMP or chlorobenzene solvates, respectively.

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in the crystal lattice. The molecules of **1** occupy a site of crystallographic inversion symmetry. The porphyrin ligand is centrosymmetric, so the four porphyrin nitrogens are rigorously coplanar. The Mn$\equiv$N moiety is statistically disordered about the inversion center with the Mn $\rightarrow$ N vector approximately normal to the N_4 plane as shown in the ORTEP diagram (Figure 1). The porphyrin core is remarkably planar with no deviations of the core atoms of more than 0.06 Å from the N_4 plane. The Mn atom is 0.388 Å out of the N_4 plane. The critical distances (Å) are as follows: Mn–N1 = 2.022 (2), Mn–N1′ = 2.021 (2), Mn–N2 = 1.983 (2), Mn–N2′ = 2.060 (2), Mn–N3(nitride) = 1.515 (3) Å. This Mn$\equiv$N(nitride) bond distance is the same as that found in the porphodimethenenitridomanganese(V) structure (1.512 (2) Å)[8] and is shorter than all other Mn$\equiv$N bonds reported in the literature.

Gel permeation chromatography (THF–BioBeads S-X3) establishes that **1** and the more soluble complex, NMn^{V}T*p*TP, are monomeric in solution. The infrared spectrum of NMn^{V}TPP displays a band at 1036 cm^{-1} for the Mn$\equiv$N stretching fundamental that shifts to a shoulder at 1008 cm^{-1} upon substitution with ^{15}N. Absent in the infrared spectra of the nitride complexes are any characteristic porphyrin π-cation radical bands (TPP$\cdot^{+}$) at 1270–1290 cm^{-1}.[13] The ^{1}H NMR line widths and chemical shifts of **1** and NMn^{V}T*p*TP establish that the nitride complexes are diamagnetic.[14] All the above evidence is in accord with a low-spin d^2 Mn(V) neutral porphyrin ground electronic state for these nitride complexes.

The quantitative electronic specrum of NMn^{V}TPP, compared with representative Mn^{IV}TPP and Mn^{III}TPP complexes in Figure 2, is a classical "normal" metalloporphyrin spectrum.[15] The principal bands in the visible spectrum, the B or Soret band (λ_{max} 424 nm) and the Q band (λ_{max} 538 nm) are π,π^* in origin and minimally perturbed by high-energy $a_{1u}(\pi),a_{2u}(\pi) \rightarrow e_g(d_\pi)$ charge-transfer (CT) transitions. The published visible spectra of the isoelectronic O=Cr^{IV}TPP complex[16,17] shows similar but broader bands than NMn^{V}TPP, in agreement with a greater but still limited perturbation of the π,π^* bands by high-energy CT transitions in the former relative to the latter. One would also expect a greater disruption of the porphyrin-ligand-based molecular orbitals and the widths and intensities of the characteristic π,π^* bands in the O=Cr^{IV}TPP complex than in the nitride complexes, for the X-ray structure of the former[16] shows a domed porphyrin ligand and not a flat porphyrin ligand as in **1**.

Complex **1** is more thermally stable than the other high-valent Mn porphyrins previously isolated and characterized and can be recovered intact after 2 min in refluxing chlorobenzene (bp = 132 °C). When **1** is treated with $\geq$1 equiv of a strong mineral acid, e.g., triflic acid, in aprotic media, e.g., chlorobenzene or dichloromethane, it decomposes rapidly to the [Mn^{III}TPP]$^{+}$ chromophore. The complex does not react under neutral or acidic conditions to transfer its nitride nitrogen to alkanes or alkenes. The low reactivity and high formal oxidation state[18] of **1** argue for the importance of diradical and paramagnetic ground electronic states in the high-valent Mn species responsible for attack on unactivated hydrocarbons in the Mn porphyrin based oxidation systems.[3,4]

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-7909730 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society (ACS-PRF grant No. 12486-AC4), is acknowledged.

Registry No. 1·*n*-C_6H_5Cl, 83632-53-5; NMn^{V}TPP, 83632-54-6; [N_3-Mn^{IV}TPP]$_2$O, 79775-62-5; ClMn^{III}TPP, 32195-55-4.

Supplementary Material Available: Tables of atomic positional and thermal parameters, bond distances and angles, and an ORTEP diagram displaying the atom numbering scheme (6 pages). Ordering information is given on any current masthead page.

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(12) The structure was solved at the U.C. Berkeley X-ray Crystallographic Facility (CHEXRAY) by a combination of vector methods, direct methods, and brute force. Equipment at CHEXRAY and general refinement procedures used may be found in ref 6 and 7.

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(14) The ^{1}H NMR chemical shifts for **1** at 20 °C ($CDCl_3$) are as follows: δ 4.04 (s, 12 H, CH_3O), 7.23 (d. 8 H, *m*-PhH), 8.04, (d, 8 H, *o*-PhH), 8.93 (s, 8 H, β-pyrrole H). At this temperature the phenyl groups are freely rotating on the NMR time scale, and the doublets arise from the coupling of adjacent *o*-PhH and *m*-PhH protons.

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Talaromycins: Application of Homonuclear Spin Correlation Maps to Structure Assignment

David G. Lynn,* Nancy J. Phillips, William C. Hutton, and Jeffrey Shabanowitz

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

D. I. Fennell and R. J. Cole

National Peanut Research Laboratory
Dawson, Georgia 31742

Received May 28, 1982

Poultry house litter, which may consist of sawdust, wood shavings, or peanut hulls with accumulated chicken manure, feathers, and wasted food, has been successfully used as a part of livestock diet.[1,2] A toxicogenic fungus identified as *Talaromyces stipitatus* has been isolated from a wood-shavings-based chicken litter.[3] The culturing of this fungus has allowed for the isolation of the toxic metabolite. We describe the application of proton homonuclear correlation spectroscopy (COSY) to the structure assignment of this metabolite.

Cultures of *T. stipitatus* in 45 Fernback flasks (2.8 L) each containing 200 mL of mycological broth (Difco Laboratories) at pH 4.8 supplemented with 15% sucrose and 2% yeast extract were kept at 27 °C for 18 days. The cultures were homogenized and filtered through cheesecloth, and the filtrate was extracted with $CHCl_3$. This dried organic layer was applied directly to silica gel (9.5 × 17 cm) and sequentially eluted with hexanes, benzene, ethyl ether, chloroform, ethyl acetate, and acetone. The active[3] ethyl acetate and acetone fractions were pooled, and careful gradient elution on silica gel (4.5 × 40 cm) with ethyl acetate and acetone gave 500 mg of a viscous oil possessing toxicity.

The clear oil contained no UV-absorbing chromophore. Mass spectrometric analyses, CI MS negative ion (N_2O), *m/z* 229 (M – H)$^{-}$, and positive ion (CH_4), *m/z* 213 (M + H – H_2O)$^{+}$, suggested a molecular formula of $C_{12}H_{22}O_4$ (*m/z* 213.1484, $C_{12}H_{21}O_3$ calcd 213.1491).[4] ^{1}H NMR (360 MHz, $CDCl_3$) measurements (ordinate of Figure 1) revealed an integrated proton intensity roughly twice that suggested by MS and rigorous chromatographic analysis on radial compression HPLC (10 μm of Si with $CHCl_3$/1% MeOH) suggested that the sample was isolated as an equal mixture of two components. Because a large-scale separation

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