*Inorg. Chem.* **1994,** *33,* 3191-3194

# Syntheses of Nitridomolybdenum(V) Porphyrin Complexes and the Molecular Structure of N≡Mo(TMP) (TMP = Tetramesitylporphyrin)[1]

**Ju Chang Kim,[†] William S. Rees, Jr.,[*,‡,§] and Virgil L. Goedken[‡,∥]**

Department of Chemistry, Pusan National University of Technology, 100 Yangdang-dong, Pusan, Korea 608-080, Department of Chemistry and Materials Research and Technology Center, MS B-164, The Florida State University, Tallahassee, Florida 32306-3006, and School of Chemistry and Biochemistry and School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

*Received October 14, 1993*

## Introduction

The importance of oxometalloporphyrins as versatile catalysts for oxidation reactions now is well recognized.[2] By comparison, nitrido- or imidometalloporphyrins have received little attention, particularly with respect to the reactivity of such complexes with organic compounds.[3] Nitridochromium,[4] -manganese,[5] -iron,[6] and -osmium[7] porphyrins are known and have been characterized. Further, nitridoporphyrins of the type N≡M(por) (M = Cr, Mn) have been reported to undergo nitrogen atom transfer reactions with chromium(III), manganese(III), and manganese(II) porphyrins.[8-10]

High-valent oxomolybdenum porphyrins also have been synthesized and studied with the objective that they could potentially be used as oxygen atom transfer agents in stoichiometric reactions.[11,12] However, the chemistry of the corresponding nitridomolybdenum porphyrins remains undeveloped. This lack may be attributed to the difficulties encountered in the synthesis of such complexes. The molybdenum ion is known to show a strong affinity for oxygen in its higher oxidation states (+4 to +6), and pentavalent molybdenum complexes having an oxo group have been isolated as the most frequently encountered examples.[13]

In order to obtain N≡Mo(por) complexes successfully, a synthetic approach utilizing low-valent molybdenum porphyrins as starting materials was necessary. Reported herein is a convenient and high yield synthesis of molybdenum nitridoporphyrins from $Me_3SiN_3$ and $[Mo(TPP)]_2$, $[Mo(TTP)]_2$, or MoTMP. These compounds, represented as N≡Mo(por), where "por" is the dianion of tetraphenylporphyrin (TPP), tetra-*p*-tolylporphyrin (TTP), or tetramesitylporphyrin (TMP), were characterized by UV/vis, IR, EPR, and MS, as well as X-ray crystallography.

## Experimental Section

Reactions were carried out under an atmosphere of nitrogen. Solvents were reagent grade and were stored over previously activated molecular sieves. Toluene and THF were distilled from sodium benzophenone ketyl. $Mo(CO)_6$, decalin (99 + %, GOLD LABEL), α-chloronaphthalene, and trimethylsilylazide were purchased from Aldrich Chemical Co. and used without further purification. Mesitaldehyde was synthesized via the method of Hoft *et al.*[14] Infrared spectra (Nujol mulls) were measured on a P-E Model 983 spectrophotometer. Mass spectra were obtained from a Finnigan 4510 GC/MS instrument with an INCOS data system. UV/vis spectra were recorded using a Cary 14 recording spectrophotometer. Electron paramagnetic resonance spectra were recorded on a Varian E-12 spectrometer equipped with E-101 (for X-band spectra) and E-110 (for Q-band spectra) microwave bridges. $^1H$ NMR spectra were obtained at 270 MHz on a Bruker SY 270 spectrometer.

**Molybdenum Porphyrin Dimers.** $[Mo(TPP)]_2$ and $[Mo(TTP)]_2$ were prepared according to published methods.[15] In a typical reaction, 0.3 g of $H_2TPP$ or $H_2TTP$ and 1.0 g of $Mo(CO)_6$ were suspended in 10 mL of decalin; the solution was deoxygenated by bubbling with nitrogen for 15 m and then refluxed for 24 h under nitrogen. The dark purple $[Mo(TPP)]_2$ or black $[Mo(TTP)]_2$, respectively, was obtained by cooling the reaction mixture to ambient temperature. The solid products were filtered under nitrogen to give almost quantitative yields (~90%).

Under the same reaction conditions, the sterically hindered ligand $H_2TMP$[16] afforded the monomeric purple crystalline Mo(TMP) in almost quantitative yield.[17]

**Preparation of Nitrido Molybdenum Complexes N≡Mo(TPP), N≡Mo(TTP), and N≡Mo(TMP).** The precursors $[Mo(TPP)]_2$, $[Mo(TTP)]_2$, or Mo(TMP) were used to make the corresponding nitrido complexes. The preparation of N≡Mo(TMP) is given as an illustration. A 300-mg portion of Mo(TMP) was transferred to a flame-dried test tube and sealed with a septum under nitrogen; 4 mL of deoxygenated α-chloronaphthalene (bp = 259 °C) was injected into the capped test tube, and then, 0.3 mL of trimethylsily azide was added by syringe. Finally the solution was subjected to reflux for 24 h. During the reaction, the color of the solution changed from dark purple to red-purple. The solution was cooled, filtered, and washed with acetonitrile to remove remaining α-chloronaphthalene and dried *in vacuo* to afford 100 mg of N≡Mo(TMP).

**N≡Mo(TMP).** UV/vis [$\lambda_{max}$ toluene (ε; $cm^{-1}$ $M^{-1}$)]: 410.0 ($5.67 \times 10^4$), 433 ($5.32 \times 10^5$), 562.0 ($2.67 \times 10^4$), 600.0 ($1.76 \times 10^4$). IR (Nujol, $cm^{-1}$): 1604, 1201, 1061, 1038, (Mo≡N), 1012, 952, 868, 852, 832, 803, 726, 558. MS(EI) [$m/e^+$ (relative intensity)]: 887.37 (38.48), 888.69 (20.55), 889.75 (33.29), 890.75 (46.97), 891.75 (51.48), 892.81 (58.02), 893.75 (51.95), 894.75 (32.21), 895.75 (24.80), 896.75 (15.23).

**N≡Mo(TPP) and N≡Mo(TTP)** were prepared and isolated in a similar manner.

**N≡Mo(TPP).** UV/vis: [$\lambda_{max}$ toluene (ε; $cm^{-1}$ $M^{-1}$)]: 410.5 ($3.22 \times 10^4$), 433 ($3.77 \times 10^5$), 560.5 ($1.27 \times 10^4$), 599.5 ($4.95 \times 10^3$). IR (Nujol, $cm^{-1}$): 1589, 1201, 1172, 1155, 1066, 1040 (N≡Mo), 1012, 834, 804, 748, 723, 702, 660. MS(EI) [$m/e^+$ (relative intensity)]: 720.62 (11.73), 721.62 (14.19), 722.62 (17.72), 723.69 (14.42), 724.69 (18.30), 725.69 (9.07), 726.62 (7.59).

**N≡Mo(TTP).** IR (Nujol, $cm^{-1}$): 1511, 1204, 1180, 1107, 1067, 1047 (N≡Mo, shoulder), 1012, 846, 798, 767, 726.

**Structure Solution and Refinement of N≡Mo(TMP).** Crystals of N≡Mo(TMP) were grown by slow vapor diffusion of pentane into a toluene solution of N≡Mo(TMP) at room temperature. After 1 day, well-formed crystals of N≡Mo(TMP) were obtained. A crystal approximately 0.3 × 0.3 × 0.4 mm was selected and mounted on a thin glass fiber with epoxy resin. The crystal was unprotected from the atmosphere. Geometric and intensity data were measured with an automated Enraf-Nonius CAD-4 diffractometer at ambient temperature. The unit cell parameters and orientation matrix were obtained by the least squares fit of 25 reflections. The compound crystallizes in the triclinic crystal system

---

[*] Address all manuscript correspondence to this author at Georgia Institute of Technology.

[†] Pusan National University of Technology.

[‡] The Florida State University.

[§] Georgia Institute of Technology.

[∥] Deceased December 22, 1992.

(1) Taken in part, from the Ph.D. dissertation of J.C.K. Department of Chemistry, The Florida State University, 1991.

(2) Meunier, B. *Chem. Rev.* **1992,** *92,* 1411.

(3) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983,** *105,* 2073.

(4) Groves, J. T.; Takashi, T.; Butler, W. M. *Inorg. Chem.* **1983,** *22,* 884.

(5) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982,** *104,* 7318.

(6) Wagner, W. D.; Nakamoto, K. *J. Am. Chem. Soc.* **1988,** *110,* 4044.

(7) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1980,** *102,* 198.

(8) Woo, L. K.; Goll, J. G. *J. Am. Chem. Soc.* **1989,** *111,* 3755.

(9) Woo, L. K.; Czapla, D. J.; Goll, J. G. *Inorg. Chem.* **1990,** *29,* 3916.

(10) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989,** *111,* 5955.

(11) Ledon, H.; Bonnet, M.; Lallemand, J.-Y. *J. Chem. Soc., Chem. Commun.* **1979,** 702.

(12) Ledon, H.; Bonnet, M. *J. Mol. Catal.* **1980,** *7,* 309.

(13) Matsuda, Y.; Yamada, S.; Murakami, Y. *Inorg. Chem.* **1981,** *20,* 2239.

(14) Rieche, A.; Gross, H.; Hoft, E. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 49.

(15) Yang, C. H.; Dzugan, S. J.; Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1986,** 1313.

(16) Wagner, R. M.; Lawrence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* **1987,** *27,* 3069.

(17) $^1H$ NMR ($CDCl_3$): δ 8.39(β-pyrrole, 2H, s), 7.35 (*m*-H, 1H, s), 7.26 (*m′*-H, 1H, s), 2.64 (*p*-Me, 3H, s), 2.08 (*o*-Me, 3H, s), 1.63 (*o′*-Me, 3H, s).

0020-1669/94/1333-3191$04.50/0

**Table 1.** Data Collection and Refinement Details

| | | | |
|---|---|---|---|
| formula | $C_{56}H_{52}N_5Mo$ | diffractometer | Enraf-Nonius CAD-4 |
| mol wt | 890.44 | | |
| cryst color | reflective purple | $\mu$, cm$^{-1}$ | 2.80 |
| cryst size, mm | 0.3 × 0.3 × 0.4 | scan speed, deg·min$^{-1}$ | 2 |
| crystal syst | triclinic | $2\theta$ scan range, deg | $2 < 2\theta < 50$ |
| space group | $P\bar{1}$ | scan technique | $\theta$–$2\theta$ |
| $a$, Å | 12.019(86) | data collcd | $+h, \pm k, \pm l$ |
| $b$, Å | 16.781(61) | scan width, deg | 1.8 |
| $c$, Å | 13.412(76) | weighting factor | $1/\sigma(F)$ |
| $\alpha$, deg | 93.164(3) | no. of unique data | 9623 |
| $\beta$, deg | 99.539(3) | no. of unique data with $I > 2\sigma(I)$ | 7576 |
| $\gamma$, deg | 99.360(3) | | |
| $V$, Å$^3$ | 2622.9 | std rflcns | 3 |
| $Z$ | 2 | LS variables | 559 |
| $\rho$(calc), g·cm$^{-3}$ | 1.145 | data/paras | 13.5 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.71073) | $R$, % | 6.1 |
| | | $R_w$, % | 7.1 |

**Table 2.** Positional Parameters for Non-Hydrogen Atoms

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Mo | 0.28880(5) | 0.19078(3) | 0.01612(4) |
| N1 | 0.2774(5) | 0.0846(3) | 0.0965(4) |
| N2 | 0.2979(5) | 0.2573(3) | 0.1583(4) |
| N3 | 0.2119(5) | 0.2848(3) | –0.0502(4) |
| N4 | 0.1923(5) | 0.1139(3) | –0.1098(4) |
| N5 | 0.4179(5) | 0.2074(4) | –0.0099(5) |
| C29A | 0.1427(7) | 0.0875(6) | 0.3752(7) |
| C2 | 0.2827(6) | –0.0454(4) | 0.1323(5) |
| C3 | 0.3102(7) | 0.0002(4) | 0.2214(5) |
| C4 | 0.3072(6) | 0.0816(4) | 0.1996(5) |
| C5 | 0.3301(6) | 0.1496(4) | 0.2726(5) |
| C6 | 0.3240(6) | 0.2304(4) | 0.2528(5) |
| C7 | 0.3444(7) | 0.2977(4) | 0.3286(6) |
| C8 | 0.3302(8) | 0.3643(4) | 0.2776(6) |
| C54A | 0.4204(6) | –0.0743(5) | –0.1022(6) |
| C10 | 0.2747(6) | 0.3889(4) | 0.0949(5) |
| C11 | 0.2310(6) | 0.3631(4) | –0.0064(5) |
| C12 | 0.1927(7) | 0.4137(4) | –0.0853(6) |
| C13 | 0.1499(7) | 0.3659(4) | –0.1699(6) |
| C14 | 0.1633(6) | 0.2842(4) | –0.1499(5) |
| C15 | 0.1330(6) | 0.2177(4) | –0.2193(5) |
| C16 | 0.1445(6) | 0.1385(4) | –0.2001(5) |
| C17 | 0.1067(6) | 0.0695(4) | –0.2710(5) |
| C18 | 0.1316(6) | 0.0038(4) | –0.2237(5) |
| C19 | 0.1861(5) | 0.0313(4) | –0.1230(5) |
| C20 | 0.2207(5) | –0.0180(4) | –0.0469(5) |
| C21 | 0.3562(6) | 0.1321(4) | 0.3830(5) |
| C22 | 0.4688(7) | 0.1443(5) | 0.4361(6) |
| C24 | 0.4007(8) | 0.0935(5) | 0.5841(6) |
| C25 | 0.2913(8) | 0.0827(5) | 0.5301(6) |
| C26 | 0.2662(7) | 0.1009(5) | 0.4229(5) |
| C27 | 0.5681(8) | 0.1788(7) | 0.3884(7) |
| C28 | 0.424(1) | 0.0736(7) | 0.6943(7) |
| C1 | 0.2597(6) | 0.0068(4) | 0.0537(5) |
| C30 | 0.2992(6) | 0.4798(4) | 0.1251(5) |
| C31 | 0.4126(7) | 0.5215(4) | 0.1329(6) |
| C32 | 0.4332(8) | 0.6056(5) | 0.1476(7) |
| C33 | 0.3464(9) | 0.6486(5) | 0.1569(7) |
| C34 | 0.2392(8) | 0.6068(5) | 0.1558(7) |
| C35 | 0.2113(7) | 0.5221(4) | 0.1396(6) |
| C36 | 0.5112(8) | 0.4770(6) | 0.1285(8) |
| C37 | 0.373(1) | 0.7413(5) | 0.1714(9) |
| C38 | 0.0918(8) | 0.4785(6) | 0.1376(9) |
| C39 | 0.0838(6) | 0.2326(4) | –0.3259(5) |
| C40 | 0.1582(7) | 0.2609(5) | –0.3904(6) |
| C41 | 0.1122(9) | 0.2741(6) | –0.4891(6) |
| C42 | –0.005(1) | 0.2566(7) | –0.5230(7) |
| C43 | –0.0770(9) | 0.2284(7) | –0.4586(8) |
| C44 | –0.0337(7) | 0.2168(5) | –0.3584(7) |
| C45 | 0.2857(8) | 0.2783(6) | –0.3556(7) |
| C46 | –0.052(2) | 0.274(1) | –0.6327(9) |
| C47 | –0.1160(8) | 0.1886(7) | –0.2872(9) |
| C48 | 0.2140(6) | –0.1058(4) | –0.0756(5) |
| C49 | 0.3105(6) | –0.1331(4) | –0.1010(5) |
| C50 | 0.3047(6) | –0.2185(4) | –0.1219(6) |
| C51 | 0.2095(7) | –0.2732(4) | –0.1162(6) |
| C52 | 0.1155(7) | –0.2457(4) | –0.0912(6) |
| C53 | 0.1161(6) | –0.1614(4) | –0.0702(6) |
| C9 | 0.3008(6) | 0.3386(4) | 0.1722(5) |
| C55 | 0.2095(9) | –0.3618(5) | –0.1354(8) |
| C56 | 0.0126(7) | –0.1326(6) | –0.0370(9) |
| C23 | 0.4880(7) | 0.1257(5) | 0.5362(6) |

in the space group $P\bar{1}$ (No. 2). The details of data collection are summarized in Table 1. The intensity measurements were made by a $\theta$-$2\theta$ technique at a scan rate of 2°/min. A total of 9623 reflections were measured for $2° < 2\theta < 50°$ and a total of 7576 reflections with $I > 2\sigma(I)$ were used to solve and refine the structure. The crystal structure was solved by the Patterson technique. Subsequent full-matrix least-squares refinement and difference Fourier synthesis led to the location of all nonhydrogen atoms. The structure was refined by full-matrix least-squares techniques. In the final refinement, anisotropic thermal parameters were used for all nonhydrogen atoms. The quantity minimized was $w(|F_o| - |F_c|)^2$ where the weights $w$ were taken as $1/\sigma^2(F_o)$. The final weighted and nonweighted $R$ indices were 7.1% and 6.1%, respectively. Atomic positional parameters for all non-hydrogen atoms are given in Table 2.

## Results and Discussion

The reaction of trimethylsilylazide with $[Mo(TPP)]_2$ or $[Mo(TTP)]_2$ successfully cleaved the metal–metal quadruple bonds present in the starting reagent and yielded the mononuclear species N≡Mo(TPP) and N≡Mo(TTP), in refluxing $\alpha$-chloronaphthalene (bp = 259 °C). Similarly, monomeric Mo(TMP) afforded the red purple N≡Mo(TMP). Although not isolated, either azido- or ((trimethylsilyl)imido)molybdenum porphyrins likely are present as intermediates in the preparation of these nitrido complexes. At this point, the fate of the TMS moiety is unclear; however, it does not interfere with the desired reaction outcome. All these nitridoporphyrins are soluble in toluene and benzene and insoluble in acetonitrile. The solubilities of these complexes in toluene increases in the order N≡Mo(TMP) > N≡Mo(TTP) > N≡Mo(TPP). They are stable to air, heat, and moisture in the solid state. They are, however, unstable in the presence of halogenated saturated hydrocarbon solvents, *e.g.*, methylene chloride or chloroform, yielding a green compound of presently unknown structure upon solvent evaporation. In addition to the characteristic IR bands present for a porphyrin complex, this green residue also contains an additional strong absorption at 941 cm$^{-1}$. Further characterization of this product was prevented by its extremely low solubility in typical solvents.

The mass spectra of these nitrido-molybdenum complexes exhibited parent peaks at the appropriate $m/e^+$ values [N≡Mo(TPP)$^+$, 725; N≡Mo(TMP)$^+$, 893] which correspond to the molecular weights of N≡Mo(TPP) and N≡Mo(TMP), respectively (Experimental Section). The IR spectra of these complexes contained characteristic porphyrin bands in addition to the band due to molybdenum nitrogen stretching (N≡Mo) at ~1040 cm$^{-1}$. The bands at 1038 cm$^{-1}$ [N≡Mo(TMP)], 1040 cm$^{-1}$ [N≡Mo(TPP)], and 1047 cm$^{-1}$ [N≡Mo(TTP)] were assigned to N≡Mo stretching frequencies, respectively. These bands were not observed in the starting molybdenum porphyrins, and are well-separated from those of oxometalloporphyrins (*cf.* 973–990 cm$^{-1}$),[18] which are formed easily during the molybdenum porphyrin syntheses, if proper precautions are not taken. Characteristic porphyrin $\pi$-cation radical bands (TPP$^{\bullet+}$) at 1270–1290 cm$^{-1}$ were absent in the infrared spectra of the nitride complexes[19] as were bands in the 900–1000-cm$^{-1}$ region, associated with Mo=O stretching absorptions.

The electronic spectrum of N≡Mo(TMP) is a classical "normal" metalloporphyrin spectrum. The principal bands in

---

(18) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsfrequenzen II: Nebengruppenelemente*; Georg Thieme Verlag: New York, 1986; pp 71–72.

(19) Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.

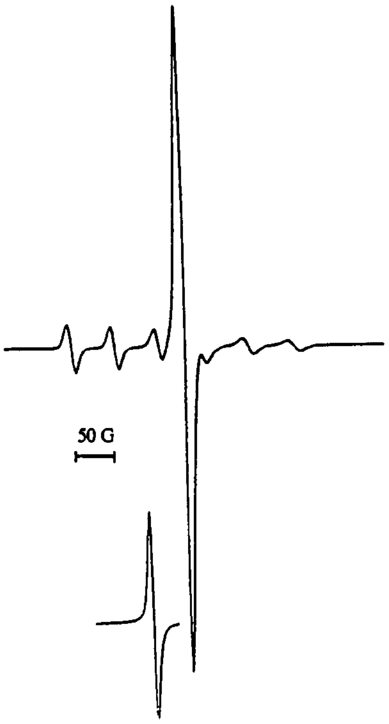

**Figure 1.** X-band EPR spectrum for N≡Mo(TMP) in toluene solution (at ambient temperature).

**Table 3.** Spin Hamiltonian Parameters for Mo(V) Complexes at Ambient Temperature, in Toluene Solution, Unless Otherwise Indicated

| complex | g | $A_{Mo}$[a] | $A_N$[a] | ref |
|---|---|---|---|---|
| N≡Mo(TPP) | 1.974 | 60.4 | *b* | this work |
| N≡Mo(TTP) | 1.976 | 61.1 | *b* | this work |
| N≡Mo(TMP) | 1.974 | 61.1 | *b* | this work |
| [Mo(NH)(TMP)][Cl] | 1.973 | 46.2 | 2.67 | this work |
| [Mo(NMe)(TPP)($H_2O$)][$I_3$] | 1.9766 | 48.58 | 2.65 | 23 |
| Mo(O)(OH)(TPP)[c] | 1.9675 | 50.0 ± 1 | 2.50 ± 0.05 | 32 |
| Mo(O)(Cl)(TPP)[c] | 1.9652 | 50.0 ± 1 | 2.50 ± 0.05 | 32 |

[a] Values in G (1 G = $10^{-4}$ T). [b] Not observed. [c] In $CH_2Cl_2$ solution.

the visible spectrum, the $\alpha$ band ($\lambda_{max}$ 600 nm), the $\beta$ band ($\lambda_{max}$ 562 nm), and the Soret band ($\lambda_{max}$ 433 nm) are $\pi$–$\pi^*$ in origin and minimally perturbed by the high-energy $a_{1u}$ ($\pi$), $a_{2u}$ ($\pi$) $\rightarrow$ $e_g$ (d $\pi$) charge transfer transition.[20] The qualitative appearances of the EPR spectra of these complexes at ambient temperature are very similar to those of other molybdenum(V) compounds (Figure 1).[21,22] The spectra are characteristic of a $d^1$ spin system. They consist of a single intense line at the center and six weaker bands over a broader range. The central intense line was assigned to the interaction of the single d electron with molybdenum nuclei ($^{92,94,96,98,100}$Mo; $\Sigma$ = 75%; $I$ = 0). The six weaker bands were assigned to the hyperfine structure caused by the interaction with $^{95}$Mo (16%) and $^{97}$Mo (10%) nuclei (both having $I$ = $^5/_2$). Superhyperfine structure, resulting from coupling with five nitrogen nuclei was not resolved. The isotropic g values are ~1.974 for all three nitridomolybdenum complexes. These are comparable to the values reported for oxomolybdenum(V) porphyrin complexes. In both cases, N≡Mo and O═Mo, the values are relatively independant of the substituents on the porphyrin rings. The observed EPR parameters for the Mo(V) nitridoporphyrins, and other related Mo(V) complexes, are given in Table 3. The substantial hyperfine constant $A_{Mo}$ (~60 G) caused by the interactino of $^{95}$Mo and $^{97}$Mo nuclei with a single d electron, coupled with the absence of an observable superhyperfine ($A_N$), supports the rather large splitting between the $d_{xy}$ orbital and the degenerate $d_{xz}$ and $d_{yz}$ orbitals, with the localization of the unpaired spin in the $d_{xy}$ orbital. This observation also is consistent with the multiply-bonded character of the nitrogen to a metal which resides above the $N_4$ plane of the porphyrin ring. The ground electronic state of these compounds is a neutral porphyrin ligand with a Mo$^{5+}$ center and presents no evidence for the alternative, that of a porphyrin $\pi$-cation radical with a Mo$^{6+}$ center.

Nitridomolybdenum porphyrins react with electrophiles such as HCl or methyl iodide. The reaction between N≡Mo(TMP) and excess $HCl_{(g)}$, saturated in *n*-pentane, occurs rapidly at ambient temperature to produce the 1:1 complex [HN=Mo(TMP)][Cl]. The loss of the N≡Mo stretching band at 1038 cm$^{-1}$ and the appearance of a new N–H stretching band at 3284 cm$^{-1}$ indicate that the nitride is the basic site and the reaction product is an imidomolybdenum porphyrin complex. Treatment of N≡Mo(TPP), under identical conditions, yielded the corresponding imido compound [HN═Mo(TPP)][Cl] (v(N═Mo) at 908 cm$^{-1}$, v(N—H) at 3341 cm$^{-1}$). When the solid [HN═Mo(TMP)][Cl] was left to stand in the air for several hours, the starting nitrido complex was recovered. However, [HN═Mo(TPP)][Cl] was not changed in the solid state over extended time periods, but it was deprotonated readily by pyridine to give the original nitrido complex. The solution EPR spectra of these protonated complexes in toluene are well resolved, and each spectrum consists of a strong 11 line multiplet due to superhyperfine coupling of five nitrogen atoms ($A_N$ = 2.67 G) to the molybdenum isotopes with $I$ = 0. Superhyperfine coupling was not resolved in the six satellite lines arising from the hyperfine interaction of the unpaired electron with $^{95,97}$Mo nuclei ($I$ = $^5/_2$). The isotropic $g$ value of 1.973 was not substantially different from that of the nitridoporphyrin compounds. However, the observed metal hyperfine coupling ($A_{Mo}$) value of 46.2 G was decreased. The decreased $A_{Mo}$ value and the observation of nitrogen superfine interaction ($A_N$) indicate that the electron density around the molybdenum atom is delocalized, when compared to N≡Mo(TMP). Alternatively, the change in the percent s character induced by the structural change from a pyramidal to a square planar structure also may contribute to this observation. Likewise, the broader signals observed may be due to a longer relaxation time. In a manner similar to that given above for HCl, methyl iodide afforded a methylimido molybdenum porphyrin upon reaction with N≡Mo(TPP).[23]

**Structure of N≡Mo(TMP).** An ORTEP representation of the solid-state structure of N≡Mo(TMP) together with the numbering scheme employed is shown in Figure 2. The molybdenum atom is coordinated with the four pyrrole nitrogen atoms and the apical nitrogen atom in a square-based pyramidal fashion, with nearly $C_{4v}$ symmetry. The molybdenum atom resides out of the porphyrin plane, towards the apical nitrogen atom. The average of the four Mo–$N_p$ interatomic distances, 2.125 Å, is at the high end of the range of bond distances observed in other pentacoordinated metalloporphyrins.[4,5,24–27] The Mo–$N_p$ distance of 2.125 Å in N≡Mo(TMP), compared to that observed in O═Mo(TTP) (2.110 Å), may reflect the strong interaction of the molybdenum atom with the nitrido ligand. This pattern of bond lengths is similar to that observed for the isoelectronic nitridochromium(V) porphyrin N≡Cr(TTP). The Cr–$N_p$ bond

---

(20) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1.

(21) Matsuda, Y.; Yamada, S.; Murakami, Y. *Chem. Lett.* **1977**, 1281.

(22) Ledon, H. J.; Bonnet, M. C.; Brigandat, Y.; Varescon, F. *Inorg. Chem.* **1980**, *19*, 3488.

(23) (a) [Mo(NMe)(TPP)($H_2O$)][$I_3$]: Kim, J. C. Ph.D. Dissertation, FSU, 1991. (b) Kim, J. C.; Rees, W. S., Jr.; Goedken, V. L. To be submitted for publication.

(24) Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.

(25) Budge, J. R.; Gatehouse, B. M. K.; Nesbit, M. C.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1981**, 370.

(26) Drew, M. G. B.; Mitchell, P. C. H.; Scott, C. E. *Inorg. Chim. Acta* **1984**, *82*, 63.

(27) Guilard, R.; Latour, J.-M.; Lecomte, C.; Marchon, J. C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1228.

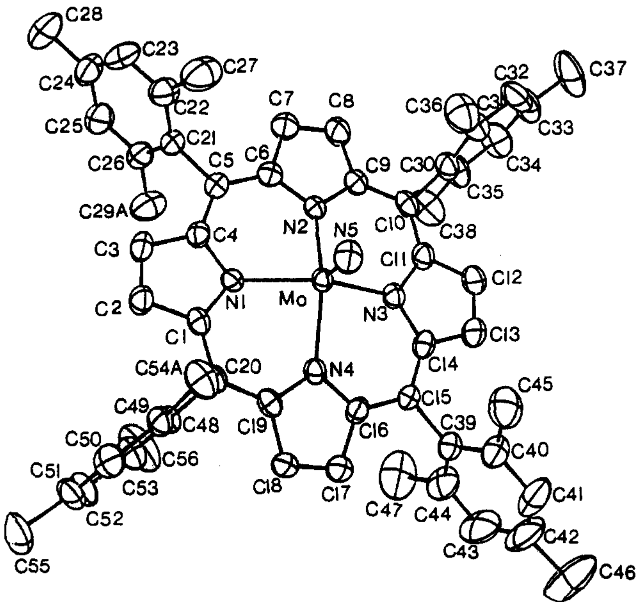

**Figure 2.** Atom labeling scheme and ORTEP representation of the solid-state structure of N≡Mo(TMP). All hydrogen atoms have been omitted for clarity of viewing the presentation. Selected bond distances (Å) and angles (deg): Mo-N1, 2.130(4); Mo-N2, 2.133(4); Mo-N3, 2.119(4); Mo-N4, 2.117(4); Mo-N5, 1.630(4); N1-Mo-N2, 86.8(1); N1-Mo-N3, 150.1(1); N1-Mo-N4, 85.5(1); N1-Mo-N5, 106.1(2); N2-Mo-N3, 86.2(1); N2-Mo-N4, 150.2(2); N2-Mo-N5, 106.1(2); N3-Mo-N4, 86.2(1); N3-Mo-N5, 103.8(2); N4-Mo-N5, 103.8(2).

distance of 2.042 Å in N≡Cr(TTP) is slightly longer than the value of 2.032 Å observed in O═Cr(TPP).[4,25] The longer Mo-N$_p$ in N≡Mo(TMP) may result from the severe out-of-plane displacement of the molybdenum atom due to the Coulombic repulsive effect between the N≡Mo group and the porphyrin ligand, thus significantly reducing the potential overlap with the molybdenum d$_{x^2-y^2}$ orbital.[28] Alternatively, the consequence of having stronger bonding interactions present between the metal center and axial ligands may weaken the interaction and thereby lead to an atomic enlongation between the metal and its other ligands. N≡Mo(TMP) displays no noticible coordination tendency at the axial site *trans* to the nitrido group. This may be explained by the well-known trans effect[29] of nitrido groups.[30] The order of trans influence is given as nitrido > oxo > imido ≫ NO and CO, and the observation of the prevelance of square pyramidal geometry for nitrido complexes, when compared with the prefered octahedral case for imido compounds, is attributed to this reason.[31] Consistent with this, the oxo group in an oxomolybdenum porphyrin [Mo(O)(Cl)(TPP)] has been reported to show a strong trans effect.[32] Even though O═Mo(TPP) takes up a monoanionic ligand at the site *trans* to the oxo group, this ligand is quite kinetically labile. The crystal structure of Mo(O)(Cl)(TPP) shows that the O═Mo distance is 1.714(3) Å and Mo—Cl bond distance is 2.494(3) Å. This Mo-Cl distance is longer that the sum of the covalent radii of Mo and Cl atoms (Mo, 1.30 Å; Cl, 0.99 Å; $\Sigma$ = 2.29 Å; ~10% enlongation observed),[33] suggesting that the Mo-Cl bond possesses a substantial fraction of ionic character.

The observed N≡Mo bond length of 1.63 Å in N≡Mo(TMP) is very short and consistent with that of a formal triple bond.[34] Other five-coordinate N≡Mo interatomic distances reported include 1.634(6) Å for [PPh$_3$Me]$_2$[MoNCl$_4$][35] and 1.63 Å for [PPh$_4$][MoNBr$_4$],[36] both of which agree quite well with that observed in the present case. In light of the structural similarity found between the oxomolybdenum complex O═Mo(TTP) and the comparable nitridomolybdenum complex N≡Mo(TMP), a comparison of their properties is warranted. From interatomic distance data, IR frequencies of O═Mo and N≡Mo, and comparison of the trans effect between oxo- and nitridomolybdenum porphyrins, it seems apparent that N$^{3-}$ is a weaker $\sigma$-acceptor and/or a stronger $\pi$-donor than O$^{2-}$ in molybdenum porphyrin systems.

**Acknowledgment.** The Department of Chemistry at The Florida State University provided partial financial support for this work.

**Supplementary Material Available:** Tables of complete bond distances and complete bond angles (6 pages). Ordering information is given on any current masthead page.

---

(28) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 709.

(29) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes, 2nd Thoroughly Revised Edition*; VCH: New York; 1991; pp 237-238.

(30) Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Yu. A. *Coord. Chem. Rev.* **1975**, *17*, pp. 1-98.

(31) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, or Alkylidyne Ligands*; Wiley: New York; 1988, pp 156-157.

(32) Ledon, H.; Mentzen, B. *Inorg. Chim. Acta* **1978**, *31*, L393.

(33) Fluck, E.; Heumann, K. G. *Periodic Table of the Elements*; VCH: Deerfield Beach, FL; 1986.

(34) Nugent, W. A., Mayer, J. A. *Metal-Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, or Alkylidyne Ligands*; Wiley: New York; 1988; p 182.

(35) Schmitte, J.; Friebel, C.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.*, **1982**, *495*, 148.

(36) Dehnicke, K.; Kruger, N.; Kujanek, R.; Weller, F. *Z. Kristallogr.* **1980**, *153*, 181.