Inorg. Chem. **1995**, *34*, 2483−2486

Synthesis and Crystal Structure of an Organoimido Molybdenum(V) Porphyrin Salt, $[Mo(NMe)(TPP)(H_2O)][I_3]$ (TPP = Tetraphenylporphyrin)[1]

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Received October 20, 1994

Introduction

Transition metal nitrido, $N{\equiv}ML_n$, imido, $HN{=}ML_n$, and organoimido, $RN{=}ML_n$, complexes each have attracted attention, not only due to an interest in their intrinsic nature[2] but also for their employment as potential reagents for nitrogen transfer[3] metal-catalyzed ammoxidation,[4] nitrogen fixation,[5] olefin aziridination,[6,7] and possible utilization for stereospecific imido group transfer to organic substrates.[8] Among the previously reported scope of organoimido complexes, which span the 3d, 4d, and 5d metals,[2] relatively few examples are known which possess chelating ligands. Although a variety of these compounds involve porphyrinato,[6,7,9−11] Schiff base derived,[12,13] or dithiocarbamato[14] ligands, organoimido metalloporphyrins are scattered, and the initial structural characterization of such a species has just appeared.[11]

Recently, the reaction of trimethylsilyl azide with low-valent Mo(II) porphyrins, resulting in the formation of nitrido Mo(V) porphyrin complexes, $N{\equiv}Mo(por)$, where "por" is the dianion of tetraphenylporphyrin (TPP) or tetramesitylporphyrin (TMP), has been described.[15] In addition, the imido derivatives were prepared by the reaction of $N{\equiv}Mo(por)$ with HCl. As one component of a continuation of the investigation of the chemistry of molybdenum porphyrins, an organoimido molybdenum porphyrin has been prepared from the reaction of $N{\equiv}Mo(TPP)$ with methyl iodide. The synthesis and crystal structure of the air stable organoimido molybdenum(V) porphyrin complex $[Mo(NMe)(TPP)(H_2O)][I_3]$ is detailed in this publication. To our knowledge, no other organoimido molybdenum porphyrin complexes have been isolated and structurally characterized.

Experimental Section

Reactions were performed under an atmosphere of nitrogen. Reagent grade benzene and toluene each were distilled from sodium benzophenone ketal and stored over previously activated molecular sieves. Methyl iodide (Aldrich) was reagent grade and used without further purification. The protonated ligand tetraphenylporphyrin (H_2TPP)[16] and the molybdenum nitrido complex $N{\equiv}Mo(TPP)$[15] were prepared according to previously published procedures. Infrared spectra of solid complexes were recorded on a Perkin-Elmer 983 infrared spectrophotometer between 4000 and 500 cm^{-1} as Nujol mulls on NaCl plates. UV/vis spectra were measured on a Cary 14 spectrophotometer, equipped with an OLIS data acquisition and manipulation workstation. Electron paramagnetic resonance spectra were recorded on a Varian E-12 spectrometer equipped with an E-101 (for X-band spectra) or E-100 (for Q-band spectra) microwave bridge. A Spectromagnetic Industries Model 5200 NMR gaussometer was used to measure the magnetic field. Elemental analyses were performed by Korea Research Institute of Chemical Technology, Taejon, Korea.

Preparation of $[Mo(NMe)(TPP)(H_2O)][I_3]$. A 25 mg portion of $N{\equiv}Mo(TPP)$ was dissolved in 3 mL of deaerated benzene. The solution was purged with a nitrogen stream for 5 min and sealed with a rubber septum under nitrogen. To this solution, an excess (0.5 mL) of methyl iodide was added via a syringe through the septum. The solution was heated for several hours at 80 °C until all of the reactants had visibly dissolved and the color of the solution had changed from purple to dark brown. Upon cooling of the reaction mixture to 10 °C for a period of several weeks, small dark brown crystals formed in nearly quantitative yield. This product occasionally contained trace quantities of byproducts, which manually were separated readily under a microscope. When the reaction was performed under similar conditions, substituting toluene as a solvent in place of benzene, dark purple $[Mo(NMe)(TPP)(H_2O)][I]$ crystallized in 3 days,[17] whose IR and UV/vis spectra qualitatively were similar to those observed for $[Mo(NMe)(TPP)(H_2O)][I_3]$.

$[Mo(NMe)(TPP)(H_2O)][I_3]$. UV/vis [$\lambda_{max}$, toluene, nm, ($\epsilon$, cm^{-1} M^{-1})]: 448 (2.33×10^5), 483 (5.84×10^4), 575 (1.97×10^4), 615 (1.39×10^4), 659 (9.09×10^3). IR (Nujol, cm^{-1}): 3300, 1590, 1567, 1293, 1276, 1233, 1201, 1173, 1153, 1069, 1015 849, 799, 752 ($RN{=}Mo$), 736, 717, 700, 662, 613. EPR (toluene, ambient temperature): central line ($I_{Mo} = 0$) $g = 1.9766$ with a six-line spectrum ($I_{Mo} = {}^5/_2$) $A_{Mo} = 48.58$ G and $A_N = 2.65$ G.

Structure Solution and Refinement of $[Mo(NMe)(TPP)(H_2O)][I_3]$. Crystals suitable for an X-ray diffraction examination were obtained from a reaction mixture which had been heated to 80 °C for 3 h and, subsequently, allowed to stand in a Dewar flask which contained 80 °C water. After slowly cooling over a several week period, the dark brown crystals were filtered from the solution and allowed to air dry. A crystal approximately 0.2 × 0.2 × 0.4 mm was selected and mounted on a glass fiber for data collection. Geometric and intensity data were measured with an automated Enraf-Nonius CAD-4 diffractometer. The unit cell parameters and orientation matrix were obtained by the least-squares fit of 25 reflections. The compound

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(17) UV/vis [λ_{max}, benzene, nm,(ϵ, cm^{-1} M^{-1})] : 450 (2.33×10^5), 575 (1.40×10^4), 613 (8.33×10^4), 650 (1.30×10^3). IR (Nujol, cm^{-1}): 3297, 1595, 1473, 1439, 1336, 1232, 1203, 1070, 1016, 798, 752($Mo{=}NR$), 717, 702, 662, 613. Anal. Calcd for $C_{46}H_{33}N_5OMoI$: C, 61.23; H, 3.74; N, 7.94. Found: C, 60.52; H, 3.55; N, 7.49.

0020-1669/95/1334-2483$09.00/0

Table 1. Crystallographic Data for [Mo(NMe)(TPP)(H_2O)][I_3] (TPP = Tetraphenylporphyrin)

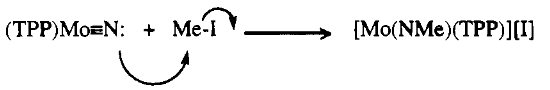
item	value
formula	$C_{45}H_{33}N_5OI_3Mo$
M_r	1167.64
space group	$P2_1/n$
colln temp	ambient
a, Å	15.610(4)
b, Å	15.794(10)
c, Å	17.519(3)
α, deg	90.00
β, deg	96.03
γ, deg	90.00
V, Å^3	4295.3
Z	4
radiation (λ, Å)	Mo Kα (0.710 73)
ϱ(calc), g·cm^{-3}	1.776
μ, cm^{-1}	24.706
R,[a] %	8.9
R_w,[b] %	8.9

[a] $R = \Sigma(|F_o| - |F_c|)^2$. [b] $R_w = \Sigma w(|F_o| - |F_c|)^2$; $w = (1/\sigma^2)(|F_o|)$.

crystallized in the monoclinic crystal system, and the space group is $P2_1/n$. The details of data collection are summarized in Table 1. The diffraction data for [Mo(NMe)(TPP)(H_2O)][I_3] were collected at ambient temperature. The intensity measurements were made by a $\theta-2\theta$ technique at the rate of 2°/min, with a scan width of 1.8°. A total of 8156 reflections were measured within $2° < 2\theta < 55°$, and a total of 7068 reflections having $I > 2\sigma(I)$ were used to solve and refine the structure. The crystal structure was solved by the Patterson technique. Subsequent full-matrix least-squares refinement and electron difference Fourier syntheses led to the location of all non-hydrogen atoms. In the final refinement anisotropic thermal parameters were used for non-hydrogen 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 for 496 LS variables were 8.9%. Atomic positional parameters for all non-hydrogen atoms are given in Table 2.

Results and Discussion

The reaction of N≡Mo(TPP) with methyl iodide yielded dark brown [Mo(NMe)(TPP)(H_2O)][I_3]. In an effort to rationalize the formation of this compound, it is necessary to invoke the involvement of solution chemistry occurring during prolonged crystallization. A plausable mechanism for the formation of this compound is presented in eq 1. Attack of the nucleophillic



$$\text{(TPP)Mo}{\equiv}\text{N:} + \text{Me-I} \longrightarrow [\text{Mo(NMe)(TPP)}][\text{I}] \quad (1)$$

nitrido ligand on methyl iodide liberates an iodide anion, which subsequently forms triiodide upon reaction with a presumed impurity of I_2. Slow crystallization of the presumably five coordinate primary reaction product [Mo(NMe)(TPP)]$^+$ resulted in the preferential formation of the triodide salt. Additionally, the remaining axial potential coordination site adventitiously ligates itself with a water molecule (eq 2).

$$[\text{Mo(NMe)(TPP)}]^+(\text{soln}) + I_3^-(\text{soln}) + H_2O(\text{soln}) \rightarrow \underset{\mathbf{1}}{[\text{Mo(NMe)(TPP)}(H_2O)][I_3]} \quad (2)$$

Upon solid state exposure of compound **1** to air for several months no visible decomposition was evidenced. Toluene solutions of the species were stable for several hours, as indicated by invariant spectroscopic data; however, it was confirmed by EPR that the complex decayed into other moieties after 2 days.

Table 2. Positional Parameters for Non-Hydrogen Atoms

atom	x	y	z
I2	0.92997(5)	0.00769(6)	0.13855(5)
I3	0.14631(8)	0.30750(8)	0.11897(8)
I1	0.04488(6)	0.16137(6)	0.12482(5)
Mo	0.28676(5)	0.34837(5)	0.39214(4)
O	0.4035(4)	0.4201(4)	0.4464(4)
N1	0.3478(5)	0.2491(4)	0.4565(4)
N2	0.3701(5)	0.3272(4)	0.3080(4)
N3	0.2588(5)	0.4675(4)	0.3425(4)
N4	0.2399(5)	0.3917(5)	0.4924(4)
N5	0.1963(5)	0.2972(5)	0.3570(4)
C1	0.4232(6)	0.2591(6)	0.3043(5)
C2	0.4583(6)	0.2603(6)	0.2317(5)
C3	0.4249(6)	0.3289(6)	0.1929(5)
C4	0.3710(5)	0.3723(5)	0.2413(4)
C5	0.3301(6)	0.4495(6)	0.2232(5)
C6	0.2784(6)	0.4939(6)	0.2710(5)
C7	0.2444(6)	0.5777(6)	0.2579(5)
C8	0.2048(6)	0.6001(6)	0.3199(5)
C9	0.2151(6)	0.5309(6)	0.3728(5)
C10	0.1860(6)	0.5312(6)	0.4464(5)
C11	0.1980(6)	0.4662(6)	0.5001(5)
C12	0.1704(6)	0.4704(7)	0.5767(5)
C13	0.1949(6)	0.3967(6)	0.6121(5)
C14	0.2393(6)	0.3451(6)	0.5592(4)
C15	0.2803(6)	0.2679(6)	0.5758(5)
C16	0.3332(6)	0.2250(6)	0.5290(5)
C17	0.3825(7)	0.1507(7)	0.5483(5)
C18	0.4266(7)	0.1321(6)	0.4914(6)
C19	0.4070(6)	0.1935(6)	0.4302(5)
C20	0.4417(6)	0.1970(6)	0.3611(5)
C21	0.5115(6)	0.1342(6)	0.3461(5)
C22	0.4886(9)	0.0554(7)	0.3169(8)
C23	0.5540(10)	0.0002(8)	0.2976(8)
C24	0.6392(10)	0.0246(9)	0.3087(7)
C25	0.6576(8)	0.1002(10)	0.3357(9)
C26	0.5948(8)	0.1580(8)	0.3575(8)
C27	0.3483(7)	0.4900(6)	0.1495(5)
C28	0.4319(8)	0.5170(7)	0.1430(6)
C29	0.4529(10)	0.5499(8)	0.0740(9)
C30	0.3906(12)	0.5584(10)	0.0159(8)
C31	0.3081(10)	0.5365(10)	0.0195(7)
C32	0.2861(8)	0.5005(8)	0.0905(6)
C33	0.1408(7)	0.6096(6)	0.4684(5)
C34	0.1858(8)	0.6810(7)	0.4896(6)
C35	0.1406(10)	0.7546(8)	0.5091(7)
C36	0.0572(11)	0.7530(8)	0.5072(7)
C37	0.0113(9)	0.6828(10)	0.4857(8)
C38	0.0517(8)	0.6117(8)	0.4684(8)
C39	0.2711(6)	0.2295(6)	0.6521(5)
C40	0.3363(7)	0.2320(8)	0.7120(6)
C41	0.3239(9)	0.1965(10)	0.7823(6)
C42	0.2505(9)	0.1628(8)	0.7959(6)
C43	0.1818(8)	0.1584(8)	0.7357(7)
C44	0.1924(7)	0.1929(7)	0.6648(6)
C45	0.1167(8)	0.2551(9)	0.3329(8)

The IR spectrum of compound **1** did not evidence the characteristic N≡Mo stretching band at 1041 cm^{-1} which was present for N≡Mo(TPP). A strong new absorption at 752 cm^{-1}, partially overlapping one of the typical porphyrin bands, is assigned to the molybdenum−imido stretching band. Undoubtedly this possesses contribribution from both M−N and N−C moieties. Absorptions at 3289 and 1567 cm^{-1} are assignable to stretching and bending vibrations of coordinated water, respectively. The band at 3289 cm^{-1} disappears upon heating compound **1** to 100 °C for a few minutes. Such behavior is consistent with the loss of molecules of coordinated water of solvation. A singular strong absorption at 1015 cm^{-1}, due to the C−H bending vibration of pyrrole rings, is suggestive of a trans orientation between the non-porphyrin ligands in compound **1**. In general, the IR spectra of tungsten and molybdenum porphyrin complexes containing a cis ligand arrangement have

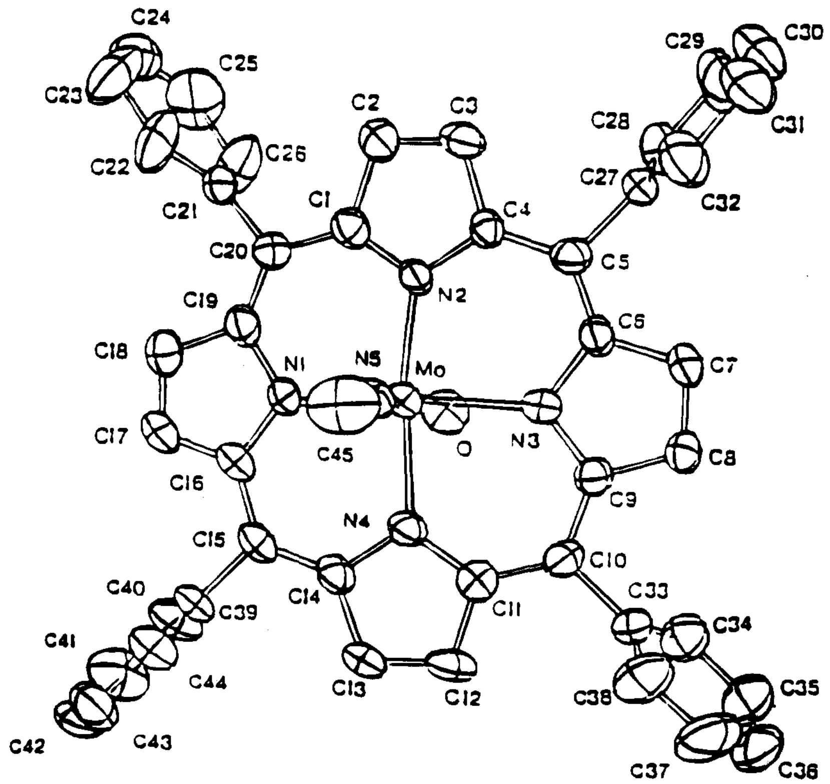


Figure 1. Atom-labeling scheme and ORTEP represention of the solid state structure of $[Mo(NMe)(TPP)(H_2O)][I_3]$ (**1**). All hydrogen atoms have been omitted for clarity of viewing the presention. Selected interatomic distances (Å) and angles (deg): Mo–N1, 2.102(6); Mo–N2, 2.096(6); Mo–N3, 2.101(6); Mo–N4, 2.089(6); Mo–N5, 1.689(6); Mo–O, 2.268(5); N1–Mo–N2, 88.70(23); N1–Mo–N3, 162.68(25); N1–Mo–N4, 88.45(23); N1–Mo–N5, 98.87(29); N1–Mo–O, 81.30(23); N2–Mo–N3,88.21(22); N2–Mo–N4, 160.74(24); N2–Mo–N5, 102.97(27); N2–Mo–O, 81.01(22); N3–Mo–N4, 88.86(23); N3–Mo–N5, 98.44(28); N3–Mo–O, 81.38(23); N4–Mo–N5, 96.29(27); N4–Mo–O, 79.73(23); N5–Mo–O, 176.01(26); Mo–N5–C45, 175.34(64).

two strong absorption peaks for the C–H bending vibration of the pyrrole ring. Such an observation has been attributed as originating from ligand distortion.[18]

The UV/vis spectrum of compound **1** displays λ_{max} at 448 (Soret), 483, 575, 615, and 659 nm. Consistent with comparison with the Soret bands of related molybdenum porphyrin complexes, the general trend is observed that trans complexes have higher Soret absorption wavelengths than those of cis complexes.[19–24] This can be understood by the quantity of $\pi-\pi^*$ energy separation differential between trans complexes and cis complexes. Generally, the extent of electron delocalization in trans complexes is higher than in cis complexes, presumably due to the greater extent of planarity present in the trans complexes. This results in a decrease of the $\pi-\pi^*$ energy separation. Thus, the observed high wavelength shift is expected in trans complexes.[25]

The ambient temperature EPR spectrum of compound **1** in toluene is typical of a d^1 configuration around the molybdenum atom. It consists of a strong central line (interaction among $^{92,94,96,98,100}Mo$ ($\Sigma = 75\%$; $I = 0$) and electron) and six weak lines (interaction among $^{95,97}Mo$ (25%; $I = {}^5/_2$) and electron). The strong central line is further split due to the interaction with four pyrrole nitrogens and one axial nitrogen (some weak signals are eclipsed under the peaks arising from the interaction between even numbered molybdenum isotopes and the electron). The isotropic g value of 1.9766 is quantatively comparable to that observed for the parent molybdenum nitrido complex, $N\equiv Mo(TPP)$. The metal hyperfine coupling constant (A_{Mo}) of 48.58 G is depressed, as compared with 60.4 G in $N\equiv Mo(TPP)$. The decreased A_{Mo} value, taken together with the observation of A_N (2.65 G), indicates that the electron density around the molybdenum atom is delocalized greater than that for $N\equiv Mo(TPP)$, and both parameters compare well with those for [Mo(NH)(TMP)][Cl] ($A_{Mo} = 46.2$ G and $A_N = 2.67$ G).[15] Such EPR similarities are not unexpected, on the basis of the qualitative similarities between HN=M and RN=M bonding and the significant differences anticipated for RN=M and N≡M moieties.

Structure of $[Mo(NMe)(TPP)(H_2O)][I_3]$. An ORTEP representation of the solid state structure of compound **1**, together with the numbering scheme employed, is shown in Figure 1. The molybdenum atom is octahedrally coordinated by the four pyrrole nitrogen atoms and two axial ligands, methylimido and water. The four molybdenum–pyrrole nitrogen (N_p) interatomic distances are 2.102(6), 2.096(6), 2.101(6), and 2.089(6) Å, and the average Mo–N distance is 2.097(6) Å. This average value falls within the range of comparable reports for such a geometry, including 2.118(3) Å in Mo(O)(Cl)(TPP),[26] 2.070(3) Å in $Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)$,[27] 2.094(3) Å in $O_3Mo_2(TPP)_2$,[28] and 2.096(4) Å in $Mo(O_2)_2(TTP)$.[20] The molybdenum atom lies

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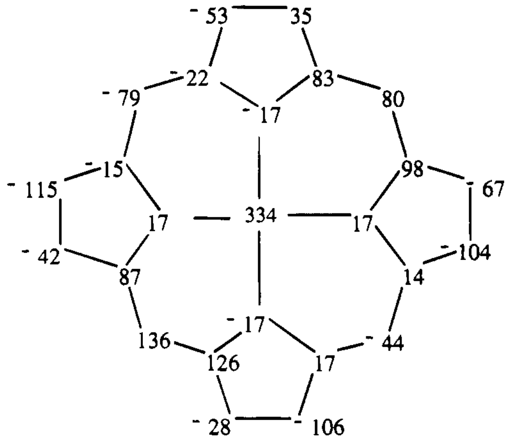

Figure 2. Diagram of the porphyrin core of [Mo(NMe)(TPP)(H_2O)]-[I_3], displaying the perpendicular displacement of each atom from the 20 atom mean plane in units of 0.001 Å. The values corresponding to the four nitrogen atoms and molybdenum atom are the perpendicular displacements from the mean plane of the four porphyrinato nitrogen atoms. The dihedral angle between the 20 atom mean plane and four nitrogen atom mean plane is 0.8°. The orientation of the structural skeleton is the same as that shown in Figure 1.

0.334 Å out of the four atom N_p plane and 0.452 Å out of the porphyrin atom core plane, toward the axial imido ligand N_i (Figure 2). The cross-plane angles (N1−Mo−N3 and N2−Mo−N4 are 162.58(25) and 160.74(24)°, respectively. The average N_p−Mo−N angle is 99.1°; thus, although the overall core is somewhat domed, there is a vaulting up of opposing pyrrole nitrogen atoms N1 and N3, toward the molybdenum atom, whereas the N2 and N4 atoms are tilted down.

The MeN=Mo distance of 1.689(6) Å observed for compound **1** is, to our knowledge, the shortest reported in imido−molybdenum systems[29−33] and ~0.03 Å longer than the O=Mo distance observed for Mo(O)(TTP).[34] Similar trends have been reported in $MoCl_2(NPh)(S_2CNEt_2)_2$, $MoOCl_2(S_2CNEt_2)_2$, TaO-(N-*i*-Pr_2)$_3$, and Ta(N-*t*-Bu)(NMe_2)$_3$ systems.[14,35−37] The covalent radius of N (70 pm) is larger than that of O (66 pm), contributing to this observation. The molybdenum−oxygen distance determined for coordinated water, 2.268(5) Å, compares well with that previously reported for $[MoO(H_2O)(CN)_4]^{2-}$ [2.271(4) Å], which strongly is supportive of the absence of an Mo−OH bond. In general, the Mo−O distance for H_2O is longer (~0.25 Å) than the Mo−O distance found for OH^-.[38] It appears at this point that repulsions between the axial H_2O ligand and the four N_p atoms are the primary contributors to the observed distance between the Mo center and the oxygen atom of the water molecule. As previously discussed for nitrido molybdenum(V) porphyrins,[15] a strong trans effect and steric repulsion between a methyl imido ligand and four N_p atoms may induce a displacement of the molybdenum atom toward the axial methyl imido ligand, thereby creating a dome with the four N_p atoms. A consequence of this structural distortion is the creation of some difficulty for the water molecule to approach the molybdenum atom closely. Presumably, any closer interaction between the water of solvation's lone electron pairs on the oxygen atom and the metal center is inhibited by the presence of repulsions between the four N_p atoms and the ligand's spatial volume.

Structural determination of compound **1** is significant in that it permits direct comparison between three similar π-donor ligands, namely, nitrido, oxo, and imido. On the basis of interatomic distances and IR frequencies {1.630(4) Å, 1038 cm^{-1} (ν(N≡Mo)) in MoN(TMP);[15] 1.656(6) Å, 970 cm^{-1} (ν(O=Mo)) in MoO(TTP);[34] 1.689(6) Å, 752 cm^{-1} (ν(RN=Mo)) in compound **1**}, it is proposed that Mo−ligand bonding decreases in the order N≡Mo > O=Mo > RN=Mo for porphyrin systems. For some time, this ordering has been debated,[39] particularly for the relative positioning between metal−oxo and metal−imido species. The three atoms C45−N5−Mo are nearly linear, with an interatomic angle of 175.34(64)°. This angle, taken together with the short MeN=Mo interatomic distance of 1.689(6) Å, supports the idea that the imido ligand acts as a four electron donor (RN=Mo).[40] Thus, in this respect, RN^{2-} resembles O^{2-} in its interactions with molybdenum porphyrin units.

Acknowledgment. The Department of Chemistry at The Florida State University provided partial financial support for this work. We appreciate a reviewer bringing ref 41 to our attention.

Supplementary Material Available: Tables of complete interatomic distances, complete interatomic angles, and complete data collection and refinement details for the solid state structure determination of [Mo(NMe)(TPP)(H_2O)][I_3] (TPP = tetraphenylpophyrin) by single crystal X-ray diffraction (5 pages). Ordering information is given on any current masthead page.

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