Molybdenum(V) on an Oxide String. Formation and Solution Stability of the Linear Complex (*μ*-*trans*-Dioxo(tetraphenylporphyrinato)molybdenato(V))-bis(oxo(tetraphenylporphyrinato)molybdenum(V)) Perchlorate

Brent J. Hamstra, Beisong Cheng, Mary K. Ellison, and W. Robert Scheidt*

The Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received May 25, 1999

The unusual linear trinuclear complex $[Mo_3O_4(TPP)_3]^+$ is formed in solution upon the reaction of $[MoO(TPP)(OClO_3)]$ with $\{[MoO(TPP)]_2O\}$, and an equilibrium between $[Mo_3O_4(TPP)_3]^+$ and its constituent species is rapidly established. Spectrophotometric experiments suggest that $[Mo_3O_4(TPP)_3]^+$ is the predominant species found in solutions resulting from the mixture of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, and its formation is strongly favored ($\log K = 5.5 \pm 0.5$ M^{-1}). No evidence of higher oligomers has been observed. A mechanism for the formation of $[Mo_3O_4(TPP)_3]^+$ by the controlled hydrolysis of $[MoO(TPP)(OClO_3)]$ is proposed.

Introduction

We recently reported the synthesis and crystallographic characterization of the novel trinuclear complex $[Mo_3O_4(TPP)_3]^+$,[1,2] which contains three molybdoporphyrin units linked by two single linear *μ*-oxo bridges. $[Mo_3O_4(TPP)_3]ClO_4$ may be obtained by the controlled hydrolysis of $[MoO(TPP)(OClO_3)]$ or by the reaction of equimolar quantities of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$. In this paper, we report spectrophotometric studies of the formation of $[Mo_3O_4(TPP)_3]ClO_4$ from $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, present data that address the formation and stability of the $[Mo_3O_4(TPP)_3]^+$ ion in solution, and discuss potential pathways for the formation of $[Mo_3O_4(TPP)_3]^+$ by direct synthesis and by the hydrolysis of $[MoO(TPP)(OClO_3)]$.

Experimental Section

General Information. Hexanes, $CHCl_3$, CH_2Cl_2, potassium hydroxide, decahydronaphthalene, and benzaldehyde were purchased from Fisher. Pyrrole and $Mo(CO)_6$ were purchased from Aldrich. Perchloric acid was purchased from GFS Chemical. Solvents used for synthesis and chromatography were used as received. For spectrophotometric measurements, CH_2Cl_2 was distilled from CaH_2. H_2TPP and $\{[MoO(TPP)]_2O\}$ were prepared by standard methods.[3,4] $[MoO(TPP)(OCH_2CH_3)]$, $[MoO(TPP)(OClO_3)]$, and $[Mo_3O_4(TPP)_3]ClO_4$ were prepared as previously described.[1] **Caution!** Although we have experienced no problems with the following procedures in dealing with systems containing perchlorate ions, they can detonate spontaneously. Such systems should be handled only in milligram quantities and should never be heated above 30 °C. Additional safety precautions are also warranted.[5] UV−visible spectra were measured on a Perkin-Elmer Lambda 19 spectrophotometer.

Solution Studies. The reaction of $[MoO(TPP)(OClO_3)]$ with $\{[MoO(TPP)]_2O\}$ was investigated utilizing a 1 mm path length Teflon-stoppered quartz mixing cell, which is illustrated in Figure S1 (Supporting Information). CH_2Cl_2 solutions of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ were each placed in one of the two 1 mm path length compartments of the cell, and the spectra (800−300 nm) of the contents of each half of the cell were individually recorded and summed. The cell was then inverted and shaken to mix the two solutions thoroughly, and the spectra of the two halves of the cell were individually recorded and summed.

To determine the stoichiometry of the predominant species formed upon mixing $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, the method of continuous variation (Job's method) was employed.[6] Equimolar CH_2Cl_2 solutions of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ were freshly prepared immediately prior to each series of experiments. From these stock solutions was prepared a series of mixed solutions such that the ratio of the initial concentrations of the two species varied, while the sum of the initial concentrations of the two species remained constant. Initial concentrations employed ranged from 134 to 200 *μ*M. UV−visible spectra of the resulting solutions were recorded from 800 to 300 nm.

Absorbance data at selected wavelengths were then used to generate plots of A^* vs the mole fraction of $[MoO(TPP)(OClO_3)]$, where $A^* = A_{obs} - \epsilon_M b[M]_i - \epsilon_D b[D]_i$, A_{obs} is the experimentally determined absorbance, ϵ_M and ϵ_D are the extinction coefficients for $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ at the selected wavelength, b is the path length of the cell, and $[M]_i$ and $[D]_i$ are the initial concentrations of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, respectively.

In the case where the stoichiometry of the predominant species is 1:1, the following equations apply:[7]

$$a = A^*/A^*_{max} = [T]/[T]_{max} \tag{1}$$

where A^*_{max} is the value of A^* when $[M]_i$ and $[D]_i$ are equal, [T] is the concentration of $[Mo_3O_4(TPP)_3]^+$ present at any given ratio of $[M]_i$ to $[D]_i$, and $[T]_{max}$ is the concentration of $[Mo_3O_4(TPP)_3]^+$ present when $[M]_i$ and $[D]_i$ are equal,

$$[T]_{max}/K = (0.5([M]_i + [D]_i) - [T]_{max})^2 \tag{2}$$

where K is the formation constant for the formation of $[Mo_3O_4(TPP)_3]^+$ from $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, and

---

* To whom correspondence should be addressed.

(1) Hamstra, B. J.; Cheng, B.; Ellison, M. K.; Scheidt, W. R. *Inorg. Chem.* **1999**, *38*, 3554.

(2) Abbreviations used in this paper: OEP, octaethylporphyrin dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion.

(3) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(4) Buchler, J. W.; Rohbock, K. *J. Inorg. Nucl. Chem. Lett.* **1972**, *8*, 1073.

(5) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335. *Chem. Eng. News* **1983**, *61* (Dec 5), 4; **1963**, *41* (July 8), 47.

(6) McBryde, W. A. E. *Talanta* **1974**, *21*, 979 and references therein.

(7) Hagenmuller, P. *C. R. Hebd. Seances Acad. Sci.* **1950**, *230*, 2190.

10.1021/ic9906003 CCC: $19.00

$$[T]/K = ((1 - x)([M]_i + [D]_i) - [T])(x([M]_i + [D]_i) - [T]) \quad (3)$$

where x is the mole fraction of $[MoO(TPP)(OClO_3)]$.

By dividing eq 3 by eq 2, setting this expression equal to a (eq 1), substituting $[T]/a$ for $[T]_{max}$, and solving the resulting expression for [T], the following equation is obtained:

$$[T] = \sqrt{((0.25a - x(1 - x))([M]_i + [D]_i))/(1 - 1/a)} \quad (4)$$

From this result, $[T]_{max}$ and K may then be calculated for each wavelength and ratio of $[M]_i$ to $[D]_i$ studied. Some calculated values of $[T]_{max}$ were found to be chemically unreasonable under the experimental conditions ($[T]_{max} > 0.5([M]_i + [D]_i)$); these values were obtained under conditions where very low concentrations of $[MoO(TPP)(OClO_3)]$ and/or $\{[MoO(TPP)]_2O\}$ would be present after mixing and were not used in the final determination of K. The log K value reported is the average of individually determined values at different wavelengths and concentrations.

Results

Figure 1 shows the UV–visible spectra of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, their spectral sum, and the spectrum of the solution that results upon mixing of the two solutions. This resulting spectrum is observed immediately upon mixing the solutions and persists without change for days. The spectrum obtained after mixing $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ differs significantly from that which would be expected if the two species did not interact. The absorbance is increased in the UV region as compared to the sum of the spectra of the individual complexes, and decreased in the visible region, particularly in the 450–480 nm region where the Soret bands of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ are observed. The observed spectrum for this mixed solution is identical within experimental error to that obtained upon dissolution of $[Mo_3O_4(TPP)_3]ClO_4$, suggesting that $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ react to form $[Mo_3O_4(TPP)_3]ClO_4$, as previously observed.[1]

At lower concentrations, the spectrum of a solution containing equimolar amounts of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ deviates from expected Beer's law behavior. The shoulder observed at ~450 nm becomes a distinct peak, and its relative intensity is increased in comparison to the intense peaks at 352 and 420 nm as the concentrations of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ decrease. These changes are consistent with decreased formation of the $[Mo_3O_4(TPP)_3]^+$ ion from $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$, as the spectrum of a solution of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ molecules that do not interact should exhibit greater absorbance in the visible region (as shown in Figure 1).

The spectra of solutions prepared with varying ratios of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ provide additional information about the formation of $[Mo_3O_4(TPP)_3]^+$. Figure 2 shows a series of spectra obtained from solutions containing different ratios of $\{[MoO(TPP)]_2O\}$ and $[MoO(TPP)(OClO_3)]$ (with the sum of the concentrations of the two complexes remaining the same), ranging from a 200 μM solution of $\{[MoO(TPP)]_2O\}$ to a solution containing 100 μM each of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$. Isosbestic behavior is observed, with isosbestic points at 492, 550, and 693 nm. Spectra obtained from solutions ranging from 100 μM each of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ to 200 μM $[MoO(TPP)(OClO_3)]$ are not cleanly isosbestic.

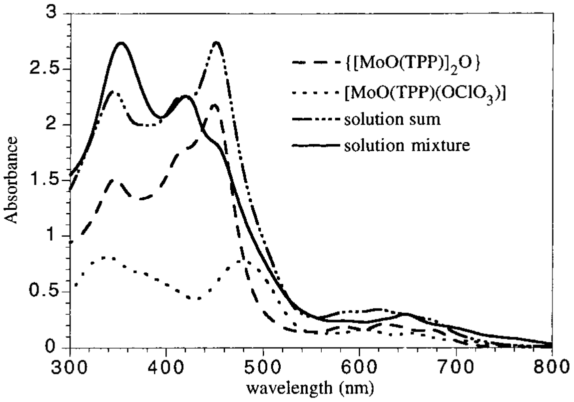

Figure 1. Spectra of 100 μM CH_2Cl_2 solutions of $\{[MoO(TPP)]_2O\}$ (– – –) and $[MoO(TPP)(OClO_3)]$ (···), their spectral sum (–···), and the spectrum obtained upon mixing the two solutions (—). Concentrations used: 200 μM $\{[MoO(TPP)]_2O\}$ (0.1 cm path length); 200 μM $[MoO(TPP)(OClO_3)]$ (0.1 cm path length); 100 μM $\{[MoO(TPP)]_2O\}$ and 100 μM $[MoO(TPP)(OClO_3)]$ (0.2 cm path length) in mixed solution (spectrum shown is the sum of the spectra of the two halves of the mixing cell after mixing; initial concentrations of the two species are 200 μM).

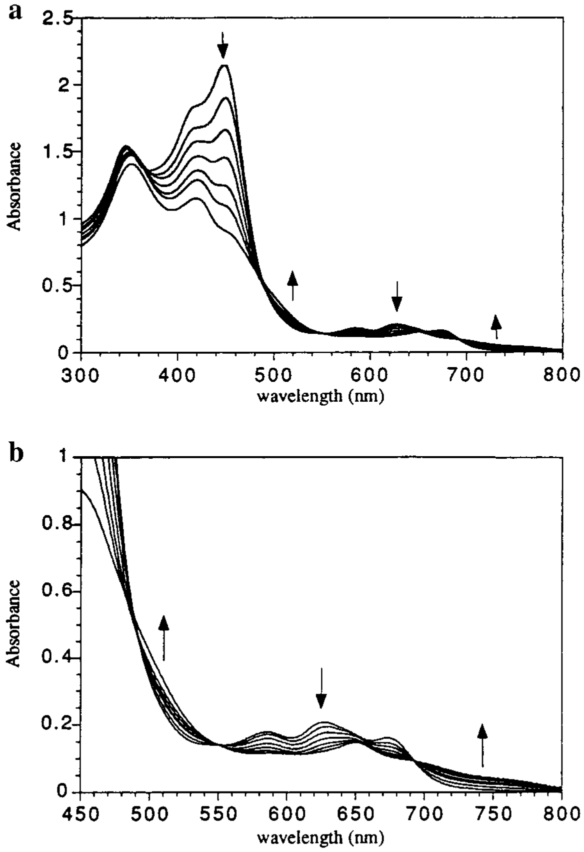

Figure 2. (a) Spectra of CH_2Cl_2 solutions containing varying concentrations of $\{[MoO(TPP)]_2O\}$ and $[MoO(TPP)(OClO_3)]$ ranging from 200 μM $\{[MoO(TPP)]_2O\}$ to 100 μM each of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ (path length 0.1 cm). For all spectra, total concentration of $[MoO(TPP)(OClO_3)] + \{[MoO(TPP)]_2O\} = 200$ μM. Arrows indicate change in absorbance upon increasing $[MoO(TPP)(OClO_3)]$ concentration. (b) Spectra shown in panel a displayed from 500 to 800 nm emphasizing isosbestic behavior.

Figure 3 gives a typical plot of A^* vs the mole fraction of $[MoO(TPP)(OClO_3)]$ for a series of spectra of solutions with different ratios of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$. This plot (and plots for experiments conducted at all other concentrations) exhibits maximal (or minimal) values of A^* at a mole fraction of 0.5, indicating that the predominant species formed upon mixture of the two species in CH_2Cl_2 solution contains a 1:1 ratio of $[MoO(TPP)(OClO_3)]$ to $\{[MoO-$

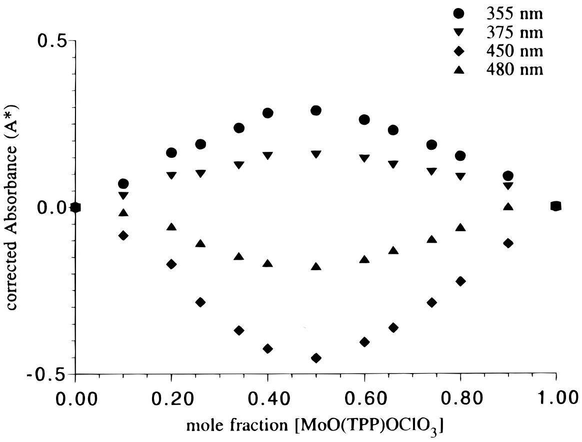

Figure 3. Plot of A^* vs the mole fraction of $[MoO(TPP)(OClO_3)]$ for the reaction of varying ratios of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$. Total concentration of $[MoO(TPP)(OClO_3)]$ + $\{[MoO(TPP)]_2O\}$ = 200 μM. Key: ●, 355 nm data; ▼, 375 nm data; ◆, 450 nm data; ▲, 480 nm data.

$(TPP)]_2O\}$. Given this result, eqs 1−4 were then employed to derive an equilibrium constant for the reaction

$$[MoO(TPP)(OClO_3)] + \{[MoO(TPP)]_2O\} \rightleftharpoons [Mo_3O_4(TPP)_3]ClO_4 \quad (5)$$

log K was determined to be 5.5 ± 0.5 M^{-1} from the data obtained at various wavelengths and concentrations.

Discussion

Spectrophotometric and crystallographic evidence suggests that $\{[MoO(TPP)]_2O\}$ and $[MoO(TPP)(OClO_3)]$ react in CH_2Cl_2 to form $[Mo_3O_4(TPP)_3]^+$ as the major product. Although this reaction has been previously shown to produce $[Mo_3O_4(TPP)_3]^+$,[1] it was not clear if the isolated, characterized solid product was the predominant species in solution. The data presented above, obtained over a range of ratios of $[MoO(TPP)(OClO_3)]$ to $\{[MoO(TPP)]_2O\}$, indicate that the predominant species in solution contains a 1:1 ratio of $[MoO(TPP)(OClO_3)]$ to $\{[MoO(TPP)]_2O\}$. These data do not distinguish between a compound containing 1 molecule each of the two complexes and compounds containing 2 (or more) of the two components; however, the isolation of only the 1:1 complex ($[Mo_3O_4(TPP)_3]ClO_4$) argues against the formation of higher nuclearity complexes with the same $[MoO(TPP)(OClO_3)]/\{[MoO(TPP)]_2O\}$ ratio.

If the formation of $[Mo_3O_4(TPP)_3]^+$ can be conceptually (and perhaps mechanistically, see below) described as the bonding of an additional $[MoO(TPP)]^+$ unit to a terminal oxo ligand of a $\{[MoO(TPP)]_2O\}$ molecule, then what prevents a second $[MoO(TPP)]^+$ unit from binding to a terminal oxo ligand in $[Mo_3O_4(TPP)_3]^+$, forming a tetranuclear 2:1 $[MoO(TPP)(OClO_3)]/\{[MoO(TPP)]_2O\}$ complex? No evidence suggests that such a complex is formed; however, the method of continuous variation indicates only the stoichiometry of the predominant complex in solution. Therefore the existence of larger complexes in small amounts cannot be definitively ruled out under the present experimental conditions. The formation of such species is, at the least, much less favorable than the formation of $[Mo_3O_4(TPP)_3]^+$ under the present conditions.

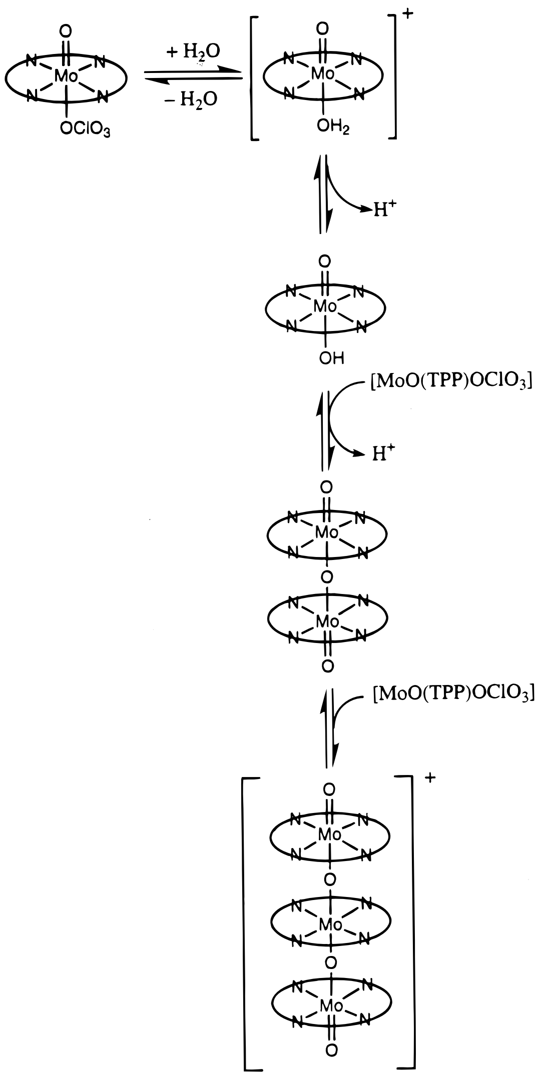

Figure 4. Proposed mechanism for the formation of $[Mo_3O_4(TPP)_3]^+$ by hydrolysis of $[MoO(TPP)(OClO_3)]$.

The log K of 5.5 ± 0.5 determined for $[Mo_3O_4(TPP)_3]ClO_4$ suggests that $[Mo_3O_4(TPP)_3]^+$ is relatively stable in solution. However, several caveats regarding this value must be noted. This value indicates that, even at the lowest concentrations used in the experiments from which this value is derived, there is at least a 75% conversion of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ into $[Mo_3O_4(TPP)_3]^+$. This estimate of $[Mo_3O_4(TPP)_3]^+$ formation is based on experiments in which the initial concentrations of the reactants are equal; where unequal concentrations are employed, the percent conversion (based upon the limiting reagent) is higher. Since the formation of $[Mo_3O_4(TPP)_3]^+$ is extensive under these conditions, only a limited set of equilibrium conditions can be examined; this may affect the accuracy of the experimentally determined stability constant K. While studying this reaction under more dilute conditions would allow us to examine a larger set of conditions and increase the accuracy of K, we were unable to do this with confidence, as we noted that solutions of $\{[MoO(TPP)]_2O\}$ did not obey Beer's law at lower concentrations.[8] The deviations observed upon dilution appeared consistent with hydrolysis of $\{[MoO(TPP)]_2O\}$, as evidenced by spectral similarities to data previously reported for the complex formulated as "[MoO(TPP)OH]".[9] We previously noted the potential for partial dissociation of $\{[MoO(TPP)]_2O\}$ into monomeric species in solution as suggested by EPR spectroscopy.[10] As stated above, spectra of

---

(8) Hamstra, B. J.; Scheidt, W. R. Unpublished observations.

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

solutions which initially contain excess [MoO(TPP)($OClO_3$)] and low concentrations of {[MoO(TPP)]$_2$O} do not exhibit isosbestic behavior. {[MoO(TPP)]$_2$O} hydrolysis at these low {[MoO(TPP)]$_2$O} concentrations may be responsible for this observation. Therefore, given that {[MoO(TPP)]$_2$O} may hydrolyze and that small amounts of higher nuclearity species may form as well, equilibria other than that described by eq 5 may be significant under these conditions. These additional equilibria may also affect the determination of K. Nonetheless, we believe that these effects are small, and that the value reported here reasonably estimates the extent of [Mo_3O_4(TPP)$_3$]$^+$ formation and its stability in solution.

Although none of these experiments directly address the mechanism of the formation of [Mo_3O_4(TPP)$_3$]$^+$ by the controlled hydrolysis of [MoO(TPP)($OClO_3$)],[1] a simple mechanism can be proposed that is consistent with these results and the analogous manganese hydrolysis chemistry.[11,12] In this mechanism, the initial step is replacement of the weakly bound perchlorato ligand of [MoO(TPP)($OClO_3$)] by water, followed by deprotonation of the resulting aquo ligand. This complex then displaces a perchlorato ligand from a second molecule of [MoO(TPP)($OClO_3$)] and is deprotonated again to form {[MoO(TPP)]$_2$O}. In this mechanism, {[MoO(TPP)]$_2$O} formation should be base-promoted; this is consistent with the previous observation that {[MoO(TPP)]$_2$O} is formed upon reaction of mononuclear molybdoporphyrin complexes with KOH.[4] For Mn complexes the second deprotonation is not observed and μ-hydroxo complexes are observed under neutral conditions. The greater Lewis acidity and π-acceptor ability of Mo(V) as compared to Mn(III) likely decreases the basicity of the bridging oxo ligand in {[MoO(TPP)]$_2$O} as compared to its Mn analogue, and therefore different kinds of complexes are isolated under the same conditions. A molecule of {[MoO(TPP)]$_2$O} may then replace a perchlorato ligand in an additional molecule of [MoO(TPP)($OClO_3$)], resulting in [Mo_3O_4(TPP)$_3$]$^+$ as independently observed in the direct nonhydrolytic reaction of [MoO(TPP)($OClO_3$)] with {[MoO(TPP)]$_2$O}. Figure 4 summarizes this proposed mechanism.

Acknowledgment. We thank the National Institutes of Health for support of this research under Grant GM-38401. We also thank Professor A. Graham Lappin for helpful discussions.

Supporting Information Available: A diagram of the spectrophotometric mixing cell, a series of spectra of equimolar mixtures of [MoO(TPP)($OClO_3$)] and {[MoO(TPP)]$_2$O} at different concentrations, and a series of spectra of mixtures of [MoO(TPP)($OClO_3$)] and {[MoO(TPP)]$_2$O} in which [MoO(TPP)($OClO_3$)] is present in excess. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9906003

---

(10) Hayes, R. G.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 1082.

(11) Cheng, B.; Cukiernik, F.; Fries, P. H.; Marchon, J.-C.; Scheidt, W. R. *Inorg. Chem.* **1995**, *34*, 4627.

(12) Cheng, B.; Fries, P. H.; Marchon, J.-C.; Scheidt, W. R. *Inorg. Chem.* **1996**, *35*, 1024.