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Molybdenum(V) on an Oxide String. Synthesis and Structure of the Novel Linear Trinuclear Complex {[MoO(TPP)][O−Mo(TPP)−O][MoO(TPP)]}ClO_4

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The syntheses and crystallographic characterization of the linear trinuclear complex $[Mo_3O_4(TPP)_3]ClO_4$ and the monomeric precursors $[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]ClO_4$ are described. The crystallographic analyses of $[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]ClO_4$ show that these similar complexes are typical oxomolybdenum(V)−porphyrin complexes whose only significant structural differences are related to their respective axial ligands. $[Mo_3O_4(TPP)_3]ClO_4$ is obtained by the controlled hydrolysis of $[MoO(TPP)(OClO_3)]$ or by the direct reaction of $[MoO(TPP)(OClO_3)]$ with $\{[MoO(TPP)]_2O\}$. This hydrolysis product contains the novel $[Mo_3O_4(TPP)_3]^+$ ion, which has an unprecedented linear $[O{=}Mo{-}O{-}Mo{-}O{-}Mo{=}O]^{7+}$ unit and three nearly parallel 24-atom porphyrin mean planes. The central porphyrin is found to be rotated 29.3° and 29.7° with respect to the two terminal porphyrin ligands, which are nearly eclipsed (twist angle 0.44°). The formation of $[Mo_3O_4(TPP)_3]ClO_4$ instead of the μ-hydroxo-bridged binuclear complexes obtained from the hydrolysis of analogous mononuclear metalloporphyrin complexes is rationalized on the basis of the greater π-acceptor ability of Mo(V). Crystal data for $[MoO(TPP)(OClO_3)\cdot 0.9CH_2Cl_2$: $a = 11.437(2)$ Å, $b = 13.567(6)$ Å, $c = 13.764(4)$ Å, $\alpha = 89.15(1)°$, $\beta = 108.86(1)°$, $\gamma = 103.96(2)°$, triclinic, space group $P\bar{1}$, $Z = 2$, $T = 293(2)$ K. Crystal data for $[MoO(TPP)(OH_2)ClO_4\cdot 1.5C_7H_8$: $a = 13.2138(7)$ Å, $b = 13.5959(12)$ Å, $c = 14.6676(11)$ Å, $\alpha = 74.292(8)°$, $\beta = 69.114(8)°$, $\gamma = 69.030(5)°$, triclinic, space group $P\bar{1}$, $Z = 2$, $T = 127(2)$ K. Crystal data for $[Mo_3O_4(TPP)_3]ClO_4\cdot C_6H_{14}\cdot 3.4CH_2Cl_2\cdot 4H_2O$: $a = 26.428(6)$ Å, $b = 18.683(6)$ Å, $c = 28.692(4)$ Å, $\beta = 113.98(2)°$, monoclinic, space group $P2_1/c$, $Z = 4$, $T = 127(2)$ K.

Introduction

The study of oxo- and hydroxo-bridged multinuclear metal complexes continues to attract the attention of numerous research groups with widely divergent interests. Since such species are present in iron-containing enzymes and metalloproteins such as ribonucleotide reductase[1] and ferritin[2] and in various manganese-containing enzymes,[3] bioinorganic chemists have been motivated to synthesize and characterize a vast array of multinuclear complexes in attempts to understand the structures and reactivity of these metalloproteins.

We have previously reported the synthesis and characterization of the binuclear μ-hydroxo-bridged porphyrin derivatives $\{[Fe(OEP)]_2(OH)\}ClO_4$,[4] $\{[Mn(OEP)]_2(OH)\}ClO_4$,[5] and $\{[Mn(TPP)]_2(OH)\}ClO_4$.[6,7] In the iron case, the μ-hydroxo-bridged complex was obtained directly by protonation of the corresponding μ-oxo-bridged species, while the analogous manganese complexes were obtained by the controlled hydrolysis of monomeric precursors. In an effort to extend this chemistry to molybdenum(V) porphyrin derivatives, we prepared the complex $[MoO(TPP)(OClO_3)]$ and attempted to utilize it as a precursor for the preparation of a hydroxo-bridged molybdenum porphyrin complex. Unexpectedly, we instead obtained the novel trinuclear complex {[MoO(TPP)][O-Mo(TPP)-O][MoO(TPP)]}ClO_4, in which the three molybdenum−porphyrin units are arranged in a linear fashion, linked by two single μ-oxo bridges. In this paper, we report the synthesis and X-ray structure of the trinuclear species {[MoO(TPP)][O−Mo(TPP)−O][MoO(TPP)]}ClO_4 (hereafter denoted as $[Mo_3O_4(TPP)_3]ClO_4$), the related monomeric species $[MoO(TPP)(OClO_3)]$, and the aquo derivative $[MoO(TPP)(OH_2)]ClO_4$.

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.[8,9] $[MoO(TPP)(OCH_2CH_3)]$ was prepared by the method of Imamura et al., with the exception that $Mo(CO)_6$ was substituted for $MoCl_5$.[10] UV/visible spectra were measured with a Perkin-Elmer Lambda 19 spectrophotometer. EPR spectra were measured on a Varian E-12 spectrometer operating at the X-band. **Caution!** Although we have experienced no problems with

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(7) Abbreviations used in this paper: OEP, octaethylporphyrin dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion; TTP, 5,10,15,20-tetratolylporphyrin dianion; TMP, 5,10,15,20-tetramesitylporphyrin dianion.

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Table 1. Crystallographic Details for [MoO(TPP)(OClO$_3$)], [MoO(TPP)(OH$_2$)]ClO$_4$, and [Mo$_3$O$_4$(TPP)$_3$]ClO$_4$

molecule	[MoO(TPP)(OClO$_3$)]·0.9CH$_2$Cl$_2$	[MoO(TPP)(OH$_2$)]ClO$_4$·1.5C$_7$H$_8$	[Mo$_3$O$_4$(TPP)$_3$]ClO$_4$·C$_6$H$_{14}$·3.4CH$_2$Cl$_2$·4H$_2$O	[Mo$_3$O$_4$(TPP)$_3$]ClO$_4$
formula	MoC$_{44}$H$_{28}$N$_4$O$_5$Cl·0.9CH$_2$Cl$_2$	MoC$_{44}$H$_{30}$N$_4$O$_6$Cl·1.5C$_7$H$_8$	Mo$_3$C$_{132}$H$_{84}$N$_{12}$O$_8$Cl·C$_6$H$_{14}$·3.4CH$_2$Cl$_2$·4H$_2$O	
fw, amu	900.53	980.31	2733.83	
a, Å	11.437(2)	13.2138(7)	26.428(6)	26.893(5)
b, Å	13.537(6)	13.5959(12)	18.683(6)	18.828(8)
c, Å	13.764(4)	14.6676(11)	28.692(4)	28.898(4)
α, deg	89.15(1)	74.292(8)		
β, deg	108.86(1)	69.114(8)	113.98(2)	114.500(14)
γ, deg	103.96(2)	69.030(5)		
V, Å^3	1952.4(11)	2267.7(3)	12 944(5)	13 315
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	2	2	4	4
D_c, g/cm^3	1.532	1.436	1.403	
μ, mm^{-1}	0.581	0.406	0.513	0.54
abs correction	DIFABS	none	none	none
radiation ($\bar{\lambda}$, Å)	Mo Kα (0.710 73)			
temp, K	293(2)	127(2)	127(2)	130(2)
R indices [$I > 2\sigma(I)$]	R1 = 0.0426, wR2 = 0.1082	R1 = 0.0488, wR2 = 0.1087	R1 = 0.0889, wR2 = 0.1878	
R indices (all data)	R1 = 0.0496, wR2 = 0.1124	R1 = 0.0597, wR2 = 0.1145	R1 = 0.1710, wR2 = 0.2524	

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.[11]

[MoO(TPP)(OClO$_3$)] and [MoO(TPP)(OH$_2$)]ClO$_4$. [MoO(TPP)(OCH$_2$CH$_3$)] (120 mg, 0.155 mmol) was dissolved in 50 mL of CH$_2$Cl$_2$, and the resulting solution was vigorously washed with two 100-mL portions of 3% aqueous HClO$_4$ in a separatory funnel. The resulting CH$_2$Cl$_2$ solution was dried with MgSO$_4$, filtered, and concentrated to ~10 mL under vacuum. The remaining solution was transferred to test tubes and layered with hexanes. Dark green single crystals were obtained after ~4 days. IR (KBr): ν(ClO$_4$) 1143 (strong), 1121 (strong), 636 (weak) cm^{-1}; ν(Mo=O) 977 cm^{-1} (strong). UV/vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ϵ, M^{-1} cm^{-1}) 341 (4.0×10^4), 375 (sh) (3.3×10^4), 482 (3.6×10^4), 605 (7.7×10^3), 655 (6.3×10^3) nm. Recrystallization of [MoO(TPP)(OClO$_3$)] from toluene led to the formation of [MoO(TPP)(OH$_2$)]ClO$_4$, which had spectral features indistinguishable from those of [MoO(TPP)(OClO$_3$)].

[Mo$_3$O$_4$(TPP)$_3$]ClO$_4$. Method 1. [MoO(TPP)(OClO$_3$)] (50 mg, 0.061 mmol) was dissolved in 50 mL of CH$_2$Cl$_2$, and the resulting solution was washed vigorously with two 250-mL portions of deionized water. The resulting CH$_2$Cl$_2$ solution was dried with MgSO$_4$, filtered, and concentrated to ~8 mL under vacuum. The remaining solution was transferred to test tubes and layered with hexanes. Large black platelike single crystals were obtained after ~4 days.

Method 2. [MoO(TPP)(OClO$_3$)] (8.3 mg, 0.010 mmol) and {[MoO(TPP)]$_2$O} (14.7 mg, 0.010 mmol) were added to a test tube and dissolved in ~4 mL of CH$_2$Cl$_2$. The resulting solution was layered with hexanes. Large black platelike single crystals were obtained after ~4 days. IR (KBr): ν(ClO$_4$) 1122 cm^{-1} (strong); ν(Mo−O) 618, 568 cm^{-1} (strong). UV/vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (ϵ, M^{-1} cm^{-1}) 352 (1.4×10^5), 420 (1.1×10^5), 450 (sh) (9.1×10^4), 648 (1.4×10^4) nm.

X-ray Structure Determinations. A brief summary of crystal data and data collection parameters for all structures reported herein is given in Table 1. Suitable crystals of [MoO(TPP)(OClO$_3$)], [MoO(TPP)(OH$_2$)]ClO$_4$, and [Mo$_3$O$_4$(TPP)$_3$]ClO$_4$ were examined on an Enraf-Nonius FAST area-detector diffractometer with a Mo rotating anode source ($\bar{\lambda}$ = 0.710 73 Å). Our detailed methods and procedures for small-molecule X-ray data collection with the FAST system have been described previously.[12] The possibility of crystal decay was excluded by comparison of a common portion of data collected after each sweep during data collection. Data were corrected for Lorentz and polarization factors. All structures were solved by direct methods with the SHELXS-86 program and were refined against F^2 with the SHELXL-93 program.[13] For [MoO(TPP)(OClO$_3$)], at the final stages of analysis, a modified version of the absorption correction program DIFABS was applied.[14,15] Unless otherwise noted, all hydrogen atoms in the structures were idealized with the standard SHELXL-93 idealization methods. Complete details of the data collections and structures are provided in the Supporting Information.

[MoO(TPP)(OClO$_3$)]. The perchlorato ligand was found to be disordered over two positions which differed only in the positions of the chlorine atom and one of the three unligated oxygen atoms (the two positions are thus defined by Cl(1a), O(2), O(3), O(4), O(5a) and Cl(1b), O(2), O(3), O(4), O(5b)). The occupancies for the two positions were initially estimated from least-squares refinements and fixed at 0.9 and 0.1, respectively. The CH$_2$Cl$_2$ solvate site was determined to be partially occupied and disordered with respect to one of the two chlorine atoms (conformations Cl(2)−C−Cl(3a) and Cl(2)−C−Cl(3b)), with occupancies fixed at 0.9 for C and Cl(2), 0.8 for Cl(3a), and 0.1 for Cl(3b).

[MoO(TPP)(OH$_2$)]ClO$_4$. The two hydrogen atoms of the aquo ligand (H(a) and H(b)) were located during solution of the structure and allowed to refine isotropically. One toluene solvent molecule was found with full site occupancy and no disorder; the other was centered on an inversion center and found to be disordered with respect to the orientation of the methyl group. The atoms of this group (C(t8), H(t8a), H(t8b), and H(t8c)) were refined with an occupancy factor of 0.5 (the other positions of these atoms in the crystal are generated by inversion).

[Mo$_3$O$_4$(TPP)$_3$]ClO$_4$. Because of the large size of the unit cell, it was necessary to collect data at a larger detector-to-crystal distance than normal. Accordingly, two different detector settings, with requisite adjustments in X-ray power, were employed in order to collect sufficient data for a satisfactory structure solution and refinement. A scale factor was applied to the low-angle data to account for the difference in applied power. The data recorded at both settings were merged into a single data set prior to solution and refinement of the structure. Data out to a θ limit of 31.8° were measured.

Extensive disorder involving the perchlorate ion and solvent molecules was observed. The perchlorate ion was found to partially

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[14] The process is based on an adaptation of the DIFABS logic[15] to area detector geometry by A. I. Karaulov, School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, Cardiff CF1 3TB, U.K. Personal communication.

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occupy two distinct positions whose total occupancy was constrained to be 1. The first perchlorate ion position (Cl(1), O(5), O(6), O(7), O(8)) was found together with residual electron density assigned as two water molecules (O(w2) and O(w3)). The constraint that the occupancy sum for the three molecules be equal to 1 was applied, and the resulting occupancies for ClO_4^-, O(w2), and O(w3) were determined to be 0.491(5), 0.378(18), and 0.131(16), respectively. The second perchlorate ion position (Cl(2), O(9), O(10), O(11), O(12)) was also found together with residual electron density assigned as two water molecules (O(w4) and O(w5)), but in this case the constraints applied were that the sum of the occupancy factors for ClO_4^- and O(w4) be equal to 1 and that the occupancy factors for O(w4) and O(w5) be equal to each other. This yielded occupancies for ClO_4^-, O(w4), and O(w5) of 0.509(5), 0.491(5), and 0.491(5), respectively. An additional partially occupied water molecule independent of any other counterion or solvent sites (O(w1)) was found with an occupancy factor of 0.118-(19).

Six CH_2Cl_2 solvate sites were found, all of which exhibited disorder and/or partial site occupancy. The first CH_2Cl_2 site was partially occupied and disordered between two geometries (Cl(3a)−C(8)−Cl-(4a) and Cl(3b)−C(8)−Cl(4b)). The occupancy of the CH_2Cl_2 molecule was fixed at 0.8, and the occupancy factors for the two geometries were determined to be 0.510(11) and 0.290(11), respectively. The second CH_2Cl_2 site exhibited a full CH_2Cl_2 molecule with three distinct positions of the carbon atom (C(9a), C(9b), and C(9c)) and four distinct chlorine atom positions (Cl(5a), Cl(5b), Cl(6a), and Cl(6b)). This resulted in three geometries for the CH_2Cl_2 molecule (Cl(5a)−C(9a)−Cl(6a), Cl(5a)−C(9b)−Cl(5b), and Cl(5b)−C(9c)−Cl(6b)), with occupancies of 0.410(6), 0.334(9), and 0.256(7), respectively. The third CH_2Cl_2 site contained two geometries (Cl(7)−C(10)−Cl(8a) and Cl-(7)−C(10)−Cl(8b)) and additional electron density that was modeled as water molecules O(w6), O(w7), and O(w8). The occupancy of the CH_2Cl_2 molecule was fixed at 0.4 (with occupancy factors of 0.3 and 0.1 for Cl(8a) and Cl(8b), respectively), and the occupancies of O(w6), O(w7), and O(w8) were fixed at 0.6, 0.2, and 0.4. The fourth and fifth CH_2Cl_2 sites were ordered but partially occupied; occupancy factors determined for Cl(9)−C(11)−Cl(10) and Cl(11)−C(12)−Cl(12) were refined to be 0.359(6) and 0.425(7), respectively. The sixth site contained an ordered CH_2Cl_2 molecule and residual electron density modeled as two water molecules O(w9) and O(w10). The total occupancy of the site was constrained to equal 1 (for a model in which either a CH_2Cl_2 molecule or the two water molecules were present), and the occupancy factors for the water molecules were constrained to be equal. The resulting occupancies for CH_2Cl_2, O(w9), and O(w10) were 0.420(7), 0.580(7), and 0.580(7), respectively.

A hexane molecule was also found in the lattice. The six carbon atoms were found to be disordered over seven positions (C(1) through C(7)), with positions C(2) through C(6) fully occupied, yielding two geometries whose occupancy factors were determined to be 0.30(2) (geometry C(1) to C(6)) and 0.70(2) (geometry C(2) to C(7)). In the refinement of $[Mo_3O_4(TPP)_3]ClO_4$ no hydrogen atoms were included for any of the solvent molecules except for two hydrogens each on the methylene carbons C(3), C(4), and C(5) of the disordered hexane molecule.

Crystals of $[Mo_3O_4(TPP)_3]ClO_4$ utilized in the diffraction experiment that led to a successful structure refinement were prepared by method 1. A second crystalline specimen prepared by method 2 was also examined and gave unit cell parameters similar to those of the crystal obtained by method 1. Solution of the structure revealed the presence of the $[Mo_3O_4(TPP)_3]^+$ unit; however, extensive solvent disorder precluded a completely satisfactory refinement. Table 1 provides only the collection and unit cell parameters for this specimen; these data are included only to illustrate that both synthetic methods produce $[Mo_3O_4(TPP)_3]ClO_4$.

Results

Molecular Structure of [MoO(TPP)(OClO$_3$)]. The structure of [MoO(TPP)(OClO$_3$)] is shown in Figure 1. Table 2 lists selected bond lengths and angles for [MoO(TPP)(OClO$_3$)] and $[MoO(TPP)(OH_2)]^+$. The molybdenum−oxo bond distance is 1.658(2) Å, which is typical for oxomolybdenum complexes.[16] The monodentate perchlorato ligand is weakly bound at a distance of 2.379(2) Å from the Mo(V) ion and is nearly directly opposite the oxo group, yielding an O═Mo−O angle of 178.49-(2)°. The average Mo−N$_p$ bond distance is 2.079(4) Å and is also consistent with prior structural determinations for Mo(V)−porphyrin complexes.[16,17] Figure 2a illustrates the displacements of the molybdenum atom and the porphyrin atoms from the mean plane defined by the 24 atoms of the macrocycle. The Mo(V) atom is displaced 0.44 Å from the mean 24-atom porphyrin plane toward the oxo ligand. The distortion of the porphyrin ring from planarity is best described as a saddled conformation, although a significant doming in the direction of the oxo ligand also appears to be present. Such saddling distortions have been observed occasionally in *meso*-tetraarylporphyrin complexes.[18] There are no significant interactions between the symmetry-related molecules of [MoO(TPP)(OClO$_3$)] in the lattice, or between molecules of [MoO(TPP)-(OClO$_3$)] and lattice solvent.

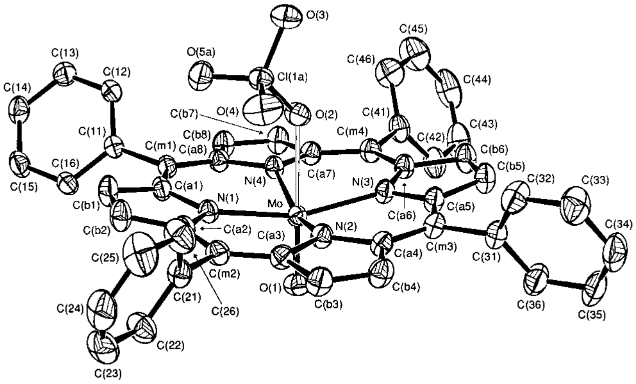

Figure 1. ORTEP diagram of [MoO(TPP)(OClO$_3$)]. Thermal ellipsoids are drawn at the 40% probability level. A complete numbering scheme for the complex is shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [MoO(TPP)(OClO$_3$)] and $[MoO(TPP)(OH_2)]^+$

[MoO(TPP)(OClO$_3$)]		$[MoO(TPP)(OH_2)]^+$	
Mo−O(1)	1.658(2)	Mo−O(1)	1.658(2)
Mo−O(2)	2.379(2)	Mo−O(2)	2.301(2)
Mo−N(1)	2.081(2)	Mo−N(1)	2.088(2)
Mo−N(2)	2.076(2)	Mo−N(2)	2.081(2)
Mo−N(3)	2.084(2)	Mo−N(3)	2.088(2)
Mo−N(4)	2.075(2)	Mo−N(4)	2.082(2)
O(1)−Mo−N(1)	99.65(9)	O(1)−Mo−N(1)	99.39(9)
O(1)−Mo−N(2)	100.66(10)	O(1)−Mo−N(2)	100.07(9)
O(1)−Mo−N(3)	99.78(10)	O(1)−Mo−N(3)	99.69(9)
O(1)−Mo−N(4)	99.81(10)	O(1)−Mo−N(4)	100.46(9)
O(1)−Mo−O(2)	178.49(8)	O(1)−Mo−O(2)	179.20(9)
N(1)−Mo−O(2)	81.34(7)	N(1)−Mo−O(2)	79.90(8)
N(2)−Mo−O(2)	80.48(8)	N(2)−Mo−O(2)	79.58(8)
N(3)−Mo−O(2)	79.22(8)	N(3)−Mo−O(2)	81.03(8)
N(4)−Mo−O(2)	79.04(8)	N(4)−Mo−O(2)	79.89(8)
N(1)−Mo−N(2)	88.62(8)	N(1)−Mo−N(2)	88.47(8)
N(1)−Mo−N(3)	160.56(8)	N(1)−Mo−N(3)	160.92(8)
N(1)−Mo−N(4)	88.62(8)	N(1)−Mo−N(4)	88.47(8)
N(2)−Mo−N(3)	88.25(8)	N(2)−Mo−N(3)	88.21(8)
N(2)−Mo−N(4)	159.53(8)	N(2)−Mo−N(4)	159.47(8)
N(3)−Mo−N(4)	87.98(8)	N(3)−Mo−N(4)	88.41(8)

Molecular Structure of [MoO(TPP)(OH$_2$)]ClO$_4$. Two $[MoO(TPP)(OH_2)]^+$ ions and their perchlorate counterions are

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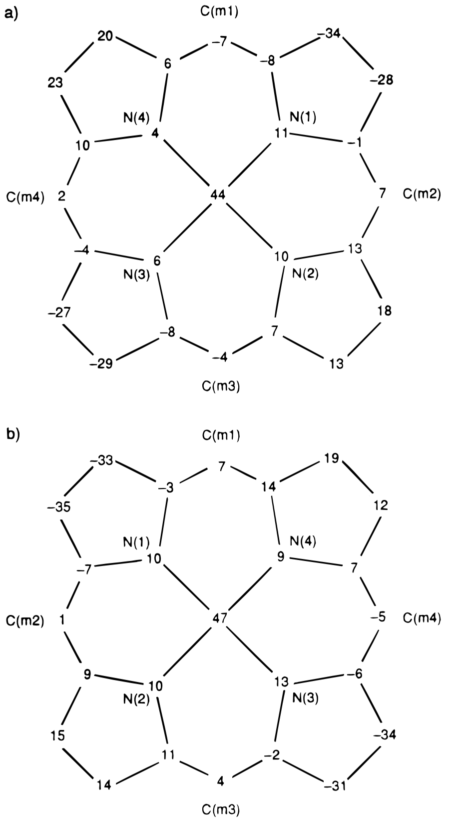

Figure 2. (a) Diagram illustrating perpendicular displacements of atoms (in units of 0.01 Å) of [MoO(TPP)(OClO$_3$)] from the mean plane defined by the 24 atoms of the porphyrin ring. A positive number indicates a displacement toward the oxo ligand. (b) Diagram illustrating perpendicular displacements of atoms (in units of 0.01 Å) of [MoO(TPP)(OH$_2$)]$^+$ from the mean plane defined by the 24 atoms of the porphyrin ring. A positive number indicates a displacement toward the oxo ligand.

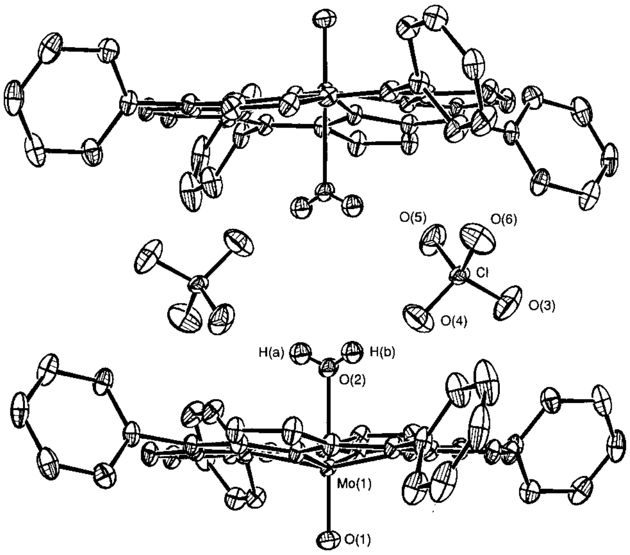

Figure 3. ORTEP diagram of two inversion-related [MoO(TPP)(OH$_2$)]$^+$ ions and their accompanying perchlorate counterions, illustrating intermolecular interactions. Thermal ellipsoids are drawn at the 50% probability level. The molybdenum atom, axial ligands, and a perchlorate counterion are labeled; the labeling scheme for the porphyrin ligand follows that described for [MoO(TPP)(OClO$_3$)] in Figure 1.

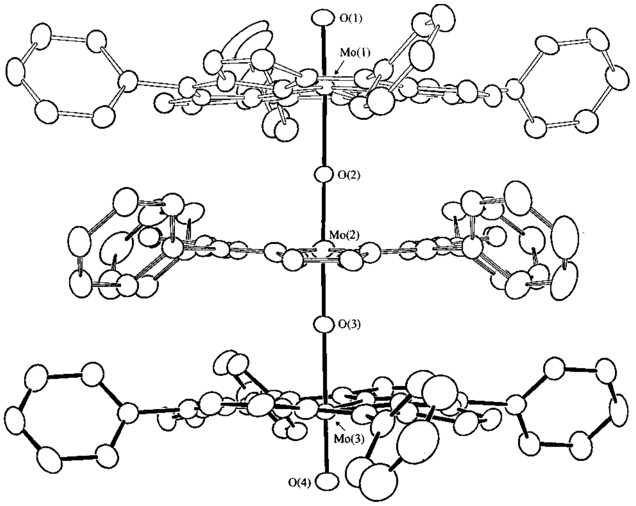

Figure 4. ORTEP diagram of [Mo$_3$O$_4$(TPP)$_3$]$^+$. Thermal ellipsoids are drawn at the 50% probability level. The molybdenum atoms and oxo ligands are labeled.

shown in Figure 3. The molybdenum−oxo bond distance is 1.658(2) Å, which is identical to that observed for [MoO(TPP)(OClO$_3$)]. The ligated water molecule is found at a distance of 2.301(2) Å from the Mo(V) ion, and again the weakly bound axial ligand is nearly directly opposite the oxo group (O═Mo−O angle = 179.20(9)°). The average Mo−N$_p$ bond distance in this complex is 2.085(3) Å, which is only very slightly longer than the corresponding distance in [MoO(TPP)(OClO$_3$)]. Figure 2b illustrates the displacements of the molybdenum atom and the porphyrin atoms from the 24-atom porphyrin mean plane. The Mo(V) atom is displaced 0.47 Å from the mean 24-atom porphyrin plane toward the oxo ligand. Again a saddled conformation most closely describes the ring distortion, and there is also some slight doming of the ring toward the oxo ligand as well.

In the crystal, the two perchlorate counterions are found within a cavity formed by two inversion-related [MoO(TPP)(OH$_2$)]$^+$ cations, and each anion bridges the two complexes via weak hydrogen bonds to the aquo ligands, as evidenced by the H(aquo)···O(perchlorate) distances of 2.02 and 2.04 Å and O(aquo)···O(perchlorate) distances of 2.765 and 2.768 Å.

Molecular Structure of [Mo$_3$O$_4$(TPP)$_3$]ClO$_4$. The structure of the [Mo$_3$O$_4$(TPP)$_3$]$^+$ cation is shown in Figure 4. Table 3 lists selected bond lengths and angles for [Mo$_3$O$_4$(TPP)$_3$]$^+$. In this complex, the numbering scheme for each porphyrin ligand is the same; the indices “1”, “2”, and “3” preceding the atom labels distinguish corresponding atoms of each crystallographically distinct ring, and the rings are numbered consecutively so that rings “1” and “3” are at the ends of the molecule and ring “2” is in the middle of the molecule.

The complex consists of a chain of three molybdoporphyrin units linked by two single μ-oxo bridges and terminated on each end by a multiply bound oxo ligand. The resulting O═Mo−O−Mo−O−Mo═O chain is essentially linear, with O−Mo−O angles of 178.0(2)°, 178.9(2)°, and 178.2(2)° and Mo−O−Mo angles of 178.7(2)° and 179.6(2)°. The identical terminal Mo═O bond lengths of 1.686(3) and 1.686(4) Å are slightly longer than the Mo═O distances in [MoO(TPP)(OClO$_3$)] and [MoO(TPP)(OH$_2$)]$^+$, but remain within the range of values expected for complexes of this type.[16] The bridging Mo−O distances fall into two groups; those involving the two peripheral molybdenum atoms average 2.100(11) Å, while the two bonds from the central molybdenum are markedly shorter, averaging 1.821(7) Å. The average Mo−N$_p$ bond distances for the two terminal porphyrin units are 2.088(2) and 2.091(7) Å, and the average Mo−N$_p$ distance for the central porphyrin is 2.096(8) Å.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_3O_4(TPP)_3]ClO_4$

Mo(1)−O(1)	1.686(3)	Mo(2)−O(2)	1.828(3)	Mo(3)−O(4)	1.686(4)
Mo(1)−O(2)	2.093(3)	Mo(2)−O(3)	1.814(3)	Mo(3)−O(3)	2.120(3)
Mo(l)−1N(1)	2.089(4)	Mo(2)−2N(1)	2.091(4)	Mo(3)−3N(1)	2.091(5)
Mo(1)−1N(2)	2.090(5)	Mo(2)−2N(2)	2.108(5)	Mo(3)−3N(2)	2.100(5)
Mo(1)−1N(3)	2.086(4)	Mo(2)−2N(3)	2.094(4)	Mo(3)−3N(3)	2.088(4)
Mo(1)−1N(4)	2.088(5)	Mo(2)−2N(4)	2.093(5)	Mo(3)−3N(4)	2.084(5)
O(1)−Mo(1)−1N(1)	94.2(2)	O(2)−Mo(2)−2N(1)	89.8(2)	O(4)−Mo(3)−3N(1)	95.3(2)
O(1)−Mo(1)−1N(2)	95.9(2)	O(2)−Mo(2)−2N(2)	89.7(2)	O(4)−Mo(3)−3N(2)	95.6(2)
O(1)−Mo(1)−1N(3)	95.9(2)	O(2)−Mo(2)−2N(3)	89.8(2)	O(4)−Mo(3)−3N(3)	95.2(2)
O(1)−Mo(1)−1N(4)	93.5(2)	O(2)−Mo(2)−2N(4)	90.9(2)	O(4)−Mo(3)−3N(4)	96.5(2)
O(1)−Mo(1)−O(2)	178.0(2)	O(2)−Mo(2)−O(3)	178.2(2)	O(4)−Mo(3)−O(3)	178.9(2)
1N(1)−Mo(1)−O(2)	84.80(14)	2N(1)−Mo(2)−O(3)	91.3(2)	3N(1)−Mo(3)−O(3)	84.0(2)
1N(2)−Mo(1)−O(2)	85.7(2)	2N(2)−Mo(2)−O(3)	88.8(2)	3N(2)−Mo(3)−O(3)	83.7(2)
1N(3)−Mo(1)−O(2)	85.1(2)	2N(3)−Mo(2)−O(3)	89.7(2)	3N(3)−Mo(3)−O(3)	85.5(2)
1N(4)−Mo(1)−O(2)	84.8(2)	2N(4)−Mo(2)−O(3)	90.6(2)	3N(4)−Mo(3)−O(3)	84.3(2)
1N(1)−Mo(1)−1N(2)	89.9(2)	2N(1)−Mo(2)−2N(2)	90.2(2)	3N(1)−Mo(3)−3N(2)	89.8(2)
1N(1)−Mo(1)−1N(3)	169.9(2)	2N(1)−Mo(2)−2N(3)	179.0(2)	3N(1)−Mo(3)−3N(3)	169.4(2)
1N(1)−Mo(1)−1N(4)	89.7(2)	2N(1)−Mo(2)−2N(4)	89.6(2)	3N(1)−Mo(3)−3N(4)	89.3(2)
1N(2)−Mo(1)−1N(3)	89.1(2)	2N(2)−Mo(2)−2N(3)	89.9(2)	3N(2)−Mo(3)−3N(3)	89.5(2)
1N(2)−Mo(1)−1N(4)	170.6(2)	2N(2)−Mo(2)−2N(4)	179.4(2)	3N(2)−Mo(3)−3N(4)	168.0(2)
1N(3)−Mo(1)−1N(4)	89.6(2)	2N(3)−Mo(2)−2N(4)	90.3(2)	3N(3)−Mo(3)−3N(4)	89.3(2)
Mo(1)−O(2)−Mo(2)	178.7(2)	Mo(2)−O(3)−Mo(3)	179.6(2)		

The displacements of the molybdenum and porphyrin atoms from the 24-atom mean plane are depicted in Figure 5. The displacements of the molybdenum atoms from the porphyrin mean planes differ significantly within the $[Mo_3O_4(TPP)_3]^+$ ion. In the two peripheral porphyrin units, the displacements are 0.08 and 0.14 Å toward the terminal oxo ligands; the internal molybdenum atom is more nearly centered within its porphyrin ring, being displaced only 0.02 Å from the 24-atom mean porphyrin plane. The conformations of the three porphyrin rings in $[Mo_3O_4(TPP)_3]^+$ are described best as saddled, with the two terminal porphyrins (shown in a and c) exhibiting slight reverse doming away from the center of the complex and toward the oxo ligand, while the central porphyrin is very nearly an ideally D_{2d}-distorted saddled conformation.

As Figure 4 indicates, the three porphyrin rings in $[Mo_3O_4(TPP)_3]^+$ are nearly parallel. The angles between the central porphyrin plane and the two terminal porphyrin planes are 1.42° and 0.84°, and the angle between the two terminal porphyrin planes is 1.82°. The central porphyrin plane is also essentially equidistant between the two terminal planes, with interplanar separations of 3.82 and 3.81 Å calculated for the distances between the central plane and the two terminal planes; the distance between the two peripheral planes is 7.63 Å (as would be expected given the virtually parallel orientations of the three planes). Figure 6 provides a view of $[Mo_3O_4(TPP)_3]^+$ looking down the O=Mo−O−Mo−O−Mo=O axis. The central ring is twisted about this axis 29.3° with respect to one terminal porphyrin and 29.7° with respect to the other, and the two terminal porphyrins are virtually eclipsed (twist angle 0.44°).

Discussion

The new complexes presented herein provide structural data that yield insight into the factors that influence the structure of oxomolybdenum−porphyrin complexes and allow us an opportunity to place the existing structural data for such complexes into a coherent framework.

The coordination environments of the molybdenum atom in $[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]^+$ are quite similar. Each has an identical Mo=O bond length of 1.658(2) Å, each exhibits a displacement of the Mo atom from the four-atom nitrogen plane of 0.36 Å, and the average Mo−N_p bond lengths of 2.079(4) Å for $[MoO(TPP)(OClO_3)]$ and 2.085(3) Å for $[MoO(TPP)(OH_2)]^+$ are almost identical as well. The only significant difference in the two is in the bond length to the sixth ligand, where the Mo−O bond length in $[MoO(TPP)(OClO_3)]$ is nearly 0.08 Å longer than in $[MoO(TPP)(OH_2)]^+$. The Mo−O($OClO_3$) bond length of 2.379(2) Å in $[MoO(TPP)(OClO_3)]$ is indicative of a very weak interaction between the Mo(V) ion and the perchlorato ligand. Surprisingly, this distance is far shorter than the Mo−Cl distance of 2.494(3) Å reported for [MoO(TPP)Cl].[19] The Mo−O bond length of 2.301(2) Å in $[MoO(TPP)(OH_2)]^+$ is slightly longer than that observed in the analogous imido complex $[Mo{=}(NCH_3)(TPP)(OH_2)]^+$ (2.268(5) Å).[20]

$[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]^+$ also exhibit similar doming and saddling distortions of the porphyrin macrocycles. This conformational combination has previously been noted for $[Mo^{IV}O(TPP)]$ and $[Mo{=}(NCH_3)(TPP)(OH_2)]^+$.[16,20] It appears that the doming of the porphyrin is caused by the displacement of the Mo atom toward the oxo ligand, which creates a tilting of the pyrrole rings upon the formation of molybdenum−nitrogen bonds. The reason for the saddling distortions in $[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]^+$ is less clear, but these distortions may be a result of an effort to decrease the steric crowding with the peripheral phenyl groups. In $[MoO(TPP)(OClO_3)]$, the angles between the four phenyl rings and the mean porphyrin plane are 48.8°, 59.7°, 66.9°, and 67.5° (average 60.7°), and in $[MoO(TPP)(OH_2)]^+$ the angles are 61.8°, 62.0°, 62.8°, and 64.3° (average 62.7°). These angles are slightly smaller than the corresponding angles in the saddled complex $[Mo^{IV}O(TPP)]$ (average 67.6°).[16]

While the structure of $[Mo_3O_4(TPP)_3]^+$ is unprecedented among metalloporphyrin complexes, its structural properties are readily understood when it is compared to analogous mononuclear and binuclear complexes. The 1.686(4) Å terminal Mo=O bonds in $[Mo_3O_4(TPP)_3]^+$ are slightly longer than the Mo=O bonds in $[MoO(TPP)(OClO_3)$ and $[MoO(TPP)(OH_2)]^+$, but somewhat shorter than the corresponding oxo−molybdenum bonds in $\{[MoO(TPP)]_2O\}$ (1.707(3) and 1.704(4) Å for two distinct crystalline forms[17,21]) and $\{[MoO(OEP)]_2O\}$ (1.721(6) Å).[22] The bridging molybdenum−oxo bond lengths involving

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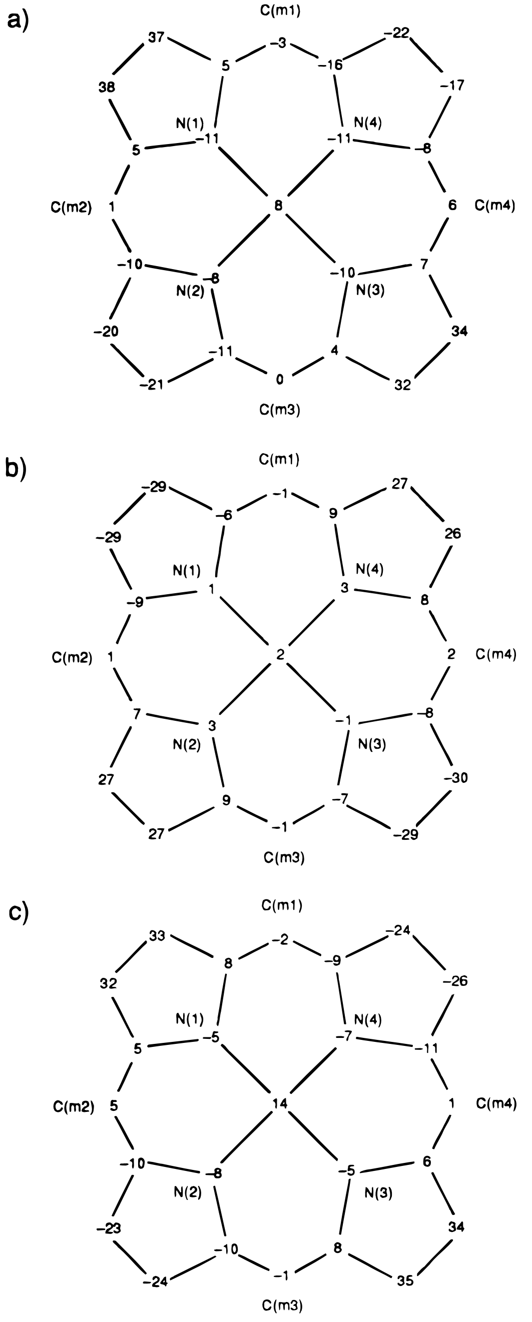

Figure 5. Diagram illustrating perpendicular displacements of atoms (in units of 0.01 Å) of $[Mo_3O_4(TPP)_3]^+$ from the mean planes defined by the 24 atoms of each porphyrin ring. For diagrams a and c, positive numbers indicate a displacement toward the terminal oxo ligand; for diagram b, a positive number indicates a displacement toward the third porphyrin ring, depicted in diagram c.

the peripheral porphyrin units measure 2.100(11) Å and are 0.2 Å or more shorter than the axial ligand distances in $[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]^+$. If one considers $[Mo_3O_4(TPP)_3]^+$ as a complex analogous to these mononuclear complexes, then $\{[MoO(TPP)]_2O\}$ is its axial ligand, and this suggests that a bridging oxo is a better ligand to oxomolybdenum(V) than ClO_4^- or water. This is due to the π-donor ability of the oxo ligand; in fact, the π-donor ability of the μ-oxo ligands in $[Mo_3O_4(TPP)_3]^+$ is such that the description of the complex as $\{[MoO(TPP)]_2O\}$ ligated to $[MoO(TPP)]^+$ is not completely accurate, as the π bonding in $[Mo_3O_4(TPP)_3]^+$ is apparently more delocalized than is suggested by such a formulation. This π bonding is also responsible for the very similar bond lengths of 1.814(3) and 1.828(3) Å from the μ-oxo ligands to the central molybdenun atom. The nearly equal distances indicate that neither oxo ligand exerts a greater trans influence than the other. Interestingly, the molybdenum–bridging oxo distances found for $\{[MoO(TPP)]_2O\}$ (1.936(3) Å)[17,21] and $\{[MoO(OEP)]_2O\}$ (1.951(1) Å)[22] are close to the average for the analogous Mo–O distances in $[Mo_3O_4(TPP)_3]^+$ (1.964 Å).

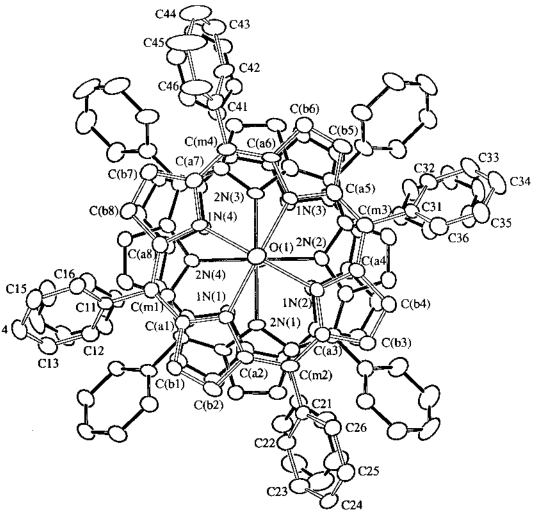

Figure 6. ORTEP diagram of $[Mo_3O_4(TPP)_3]^+$ viewed down the molybdenum–oxygen axis. Thermal ellipsoids are drawn at the 50% probability level. Porphyrin ring “1” (hollow bonds) is labeled completely; the prefix “1” is omitted from the labels for the carbon atoms. The nitrogen atoms of porphyrin ring “2” are labeled. The numbering of carbon atoms in rings “2” and “3” (solid bonds) follows the convention designated for the atoms in ring “1”.

$[Mo_3O_4(TPP)_3]^+$ and $\{[MoO(TPP)]_2O\}$ both have a nearly linear oxygen–molybdenum axis running through the center of the molecule. For $[Mo_3O_4(TPP)_3]^+$ the average O–Mo–O angle is 178.4(4)°, while for $\{[MoO(TPP)]_2O\}$ O–Mo–O angles of 178.2(2)° and 176.8(6)° (average) have been determined.[17,21] The average Mo–O–Mo angle is 179.2(5)° in $[Mo_3O_4(TPP)_3]^+$, and the Mo–O–Mo angle in $\{[MoO(TPP)]_2O\}$ has been reported as 180° and 178.5(2)°.[17,21] The corresponding angles in $\{[MoO(OEP)]_2O\}$ are all constrained by symmetry to be 180°.[22]

The arrangements of the porphyrin rings with respect to each other in $[Mo_3O_4(TPP)_3]^+$ are also quite similar to that observed for $\{[MoO(TPP)]_2O\}$. In $\{[MoO(TPP)]_2O\}$, the two porphyrin rings are parallel.[17] In $[Mo_3O_4(TPP)_3]^+$, the angles between adjacent porphyrin planes are 0.82° and 1.42°. The interplanar distances in $[Mo_3O_4(TPP)_3]^+$ are 3.82 and 3.81 Å, which are just slightly smaller than the 3.85 Å distance found in $\{[MoO(TPP)]_2O\}$,[17,21] but much larger than the 3.54 Å distance seen in $\{[MoO(OEP)]_2O\}$,[22] in which the ethyl groups are all directed away from the center of the molecule, allowing a closer porphyrin–porphyrin approach than is possible for the more bulky $\{[MoO(TPP)]_2O\}$. The porphyrin rings within $[Mo_3O_4(TPP)_3]^+$ and $\{[MoO(TPP)]_2O\}$ are twisted with respect to each other by similar amounts; the twist angles are 29.3° and 29.7° between adjacent porphyrins in $[Mo_3O_4(TPP)_3]^+$ and 30.4° and 28.6° in the two structures of $\{[MoO(TPP)]_2O\}$.[17,21] The rings in $\{[MoO(OEP)]_2O\}$ are somewhat more eclipsed (twist angle: 22.3°).[22]

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Table 4. Coordination Environments for Several Mo−Tetraarylporphyrin Complexes[a]

complex	Δ_{Mo}, Å[b]	Mo−Ax, Å	Mo=O, Å	Mo−N$_p$, Å[c]	ref
[Mo^{IV}O(TTP)]	0.64		1.656(6)	2.110(6)	16
[Mo^{V}N(TMP)]	0.55		1.630(4)[d]	2.125(7)	23
[Mo^{V}O(TPP)Cl]	0.39	2.494(3)	1.714(3)	2.118(3)	19
[Mo^{V}O(TPP)(OClO$_3$)]	0.36	2.379(2)	1.658(2)	2.079(4)	this work
[Mo^{V}O(TPP)(OH$_2$)]	0.36	2.301(2)	1.658(2)	2.085(3)	this work
[Mo^{V}(NCH$_3$)(TPP)(OH$_2$)]	0.33	2.268(5)	1.689(6)	2.097(6)	20
[Mo^{V}O(TPP)(NCS)]	0.28	2.257(4)	1.673(3)	2.086(6)	24
[Mo$^{V}_3$O$_4$(TPP)$_3$]$^+$ [e]	0.20	2.107(14)	1.686(4)	2.090(4)	this work
[Mo^{V}O(TPP)F]	0.16	1.967(9)	1.677(12)	2.089(3)	24
{[Mo^{V}O(TPP)]$_2$O}	0.09	1.936(3)	1.707(3)	2.094(3)	17
{[Mo^{V}O(TPP)]$_2$O}	0.09	1.936(16)	1.704(4)	2.096(6)	21
[Mo$^{V}_3$O$_4$(TPP)$_3$]$^+$ [f]	0.00	1.821(7)		2.097(7)	this work

[a] Numbers in parentheses are the standard uncertainties. [b] Displacement of the Mo atom from the mean four-atom porphyrin nitrogen plane. [c] Average value of reported Mo−N$_p$ bond lengths. [d] Mo=N distance. [e] Numbers given are the average values for both terminal molybdoporphyrin units. [f] Numbers given are the average values for the central molybdoporphyrin unit.

The close approach of three porphyrin rings and the different coordination environments in [Mo$_3$O$_4$(TPP)$_3$]$^+$ result in conformations of the porphyrin rings in [Mo$_3$O$_4$(TPP)$_3$]$^+$ that differ somewhat from those seen in [MoO(TPP)(OClO$_3$)] and [MoO(TPP)(OH$_2$)]$^+$. While the two terminal porphyrin rings in [Mo$_3$O$_4$(TPP)$_3$]$^+$ both exhibit the combination of doming and saddling seen in [MoO(TPP)(OClO$_3$)] and [MoO(TPP)(OH$_2$)]$^+$, there is a difference in that the doming is toward the terminal oxo ligand in the mononuclear complexes, but away from the terminal oxo ligand for the rings in [Mo$_3$O$_4$(TPP)$_3$]$^+$. This reversal of the doming in [Mo$_3$O$_4$(TPP)$_3$]$^+$ is likely caused by steric repulsion of the bulky phenyl groups of adjacent porphyrins, and the location of the Mo atom closer to the porphyrin plane makes this conformation somewhat more energetically favorable. A similar “reverse” doming is also seen in {[MoO(TPP)]$_2$O}.[17,21] As mentioned above, the central porphyrin ring in [Mo$_3$O$_4$(TPP)$_3$]$^+$ is not domed, but is saddled (as are the other two porphyrins). The phenyl rings are more nearly coplanar with the porphyrin mean plane for all three rings in [Mo$_3$O$_4$(TPP)$_3$]$^+$ than in [MoO(TPP)(OClO$_3$)] and [MoO(TPP)(OH$_2$)]$^+$; the average phenyl ring−porphyrin dihedral angles are 56.2° and 51.8° for the two terminal porphyrin units and 50.1° for the internal porphyrin. These angles are similar to the average phenyl ring−porphyrin angle in {[MoO(TPP)]$_2$O} of 56.4°.[17] The angles between closest phenyl rings on adjacent porphyrins in [Mo$_3$O$_4$(TPP)$_3$]$^+$ are close to perpendicular with average phenyl−phenyl angles of 78.6° and 82.3°. Near perpendicular orientations of adjacent phenyl groups in single-atom-bridged porphyrin dimers have been noted previously; it has been shown that perpendicular orientations are favored in complexes where the phenyl rings are packed more closely together because of smaller interplanar spacings.[6]

Table 4[23,24] lists parameters for the coordination environments of several oxomolybdenum−tetraarylporphyrin complexes. A clear correlation exists between the length of the molybdenum−axial ligand bond trans to the oxo ligand and the displacement of the molybdenum atom from the four nitrogen atom plane toward the oxo ligand. Trans ligands that form shorter bonds to molybdenum have smaller displacements of the Mo atom out of the porphyrin plane; ligands that are weakly bound to molybdenum lead to larger out-of-plane displacements. For the mononuclear oxomolybdenum−porphyrin complexes, the axial bond lengths decrease in the order Cl$^-$ > ClO$_4^-$ > H$_2$O > NCS$^-$ > F$^-$. The trend for the latter four ligands in this series is reasonably explained in terms of their relative nucleophilicities. The long Mo−Cl distance of 2.494(3) Å reported for [MoO(TPP)Cl], however, does not seem consistent with the structures of the other complexes, even when the larger size of chloride as compared to fluoride or the other relevant donor atoms is taken into account.[19]

In contrast to the values of the displacement of the Mo atom from the porphyrin plane, the Mo=O bond lengths show much less variation (Table 4). Given the extensive π bonding between the terminal oxo ligand and molybdenum, this is not particularly surprising. Still, there does appear to be a weak correlation between the bond lengths of the two axial ligands, in that a decrease in the distance between molybdenum and the weakly bound axial ligand is generally accompanied by an increase in the Mo=O bond length ([MoO(TPP)Cl] is a notable exception to this trend). The increase of Mo=O bond lengths in the order [MoO(TPP)(OH$_2$)]$^+$ < [Mo$_3$O$_4$(TPP)$_3$]$^+$ < {[MoO(TPP)]$_2$O} is probably indicative of the extent of π bonding between the bridging oxo ligand and Mo for [Mo$_3$O$_4$(TPP)$_3$]$^+$ and {[MoO(TPP)]$_2$O}, as stronger π bonding between the bridging oxo ligand and the empty d_{xz} and d_{yz} orbitals of Mo(V) should produce a weakening of the bond between molybdenum and the terminal oxo ligand.

The Mo−N$_p$ bond lengths for the six-coordinate complexes listed in Table 4 show very little difference among these compounds (with the exception of [MoO(TPP)Cl]). Since the two five-coordinate complexes [MoO(TTP)] and [MoN(TMP)] have the greatest displacements of the Mo atom from the four-atom porphyrin nitrogen plane and have Mo−N$_p$ bond lengths significantly longer than the six-coordinate complexes, one might expect that the closer proximity of Mo to the porphyrin nitrogen plane would produce increasingly shorter Mo−N$_p$ bonds within the series of complexes. This is not observed; if a correlation exists, it indicates that a closer approach by Mo toward the nitrogen plane leads to a slight increase in the Mo−N$_p$ bond length. Thus it appears that the shortening of bonds that would be produced by closer proximity of the Mo atom to the porphyrin plane is offset by an increase in the size of the core of the porphyrin macrocycle as it expands to accommodate the Mo atom.

While the [Mo$_3$O$_4$(TPP)$_3$]$^+$ ion has structural characteristics consistent with what might be expected for such a complex based on comparisons with analogous complexes, the interesting question of why [Mo$_3$O$_4$(TPP)$_3$]$^+$ should form at all is not definitively addressed by these data. Why is [Mo$_3$O$_4$(TPP)$_3$]$^+$ formed upon shaking a CH$_2$Cl$_2$ solution of [MoO(TPP)(OClO$_3$)] with water, when the same procedure carried out with analogous

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manganese complexes yields μ-hydroxo-bridged $\{[Mn(OEP)]_2(OH)\}ClO_4$[5] and $\{[Mn(TPP)]_2(OH)\}ClO_4$?[6] This difference appears to reflect the relative π bonding abilities of Mo(V) and Mn(III). Whereas Mo(V) has empty d_{xz} and d_{yz} orbitals able to act as π acceptors, facilitating strong overlap between the metal- and ligand-based π-bonding orbitals, high-spin Mn(III) has half-filled d_{xz}, and d_{yz} orbitals and is therefore a poorer π acceptor. Bridging oxo ligands in μ-oxo-bridged Mn (or Fe) dimers are then likely more basic due to this diminished π bonding by the ligands, and the μ-hydroxo complexes are thus more stable and are able to be isolated and characterized. In contrast, the Mo complexes may be less easily protonated and less stable, but may more easily form trinuclear species such as $[Mo_3O_4(TPP)_3]^+$ that are stabilized by the extensive π bonding involving terminal and bridging oxo ligands. The formation of $[Mo_3O_4(TPP)_3]^+$ by the reaction of equimolar amounts of $[MoO(TPP)(OClO_3)]$ and $\{[MoO(TPP)]_2O\}$ or by controlled hydrolysis of $[MoO(TPP)(OClO_3)]$ is consistent with the idea that extensive π bonding interactions promote formation of the trinuclear species.[25,26] Studies of the formation and stability of $[Mo_3O_4(TPP)_3]^+$ in solution have been undertaken.[27]

Summary. The syntheses of the molybdoporphyrin complexes $[MoO(TPP)(OClO_3)]$, $[MoO(TPP)(OH_2)]^+$, and $[Mo_3O_4(TPP)_3]^+$ are reported. The X-ray structures of $[MoO(TPP)(OClO_3)]$ and $[MoO(TPP)(OH_2)]^+$ are shown to be typical for six-coordinate Mo(V) porphyrin complexes, and the novel $[Mo_3O_4(TPP)_3]^+$ ion is shown to be a linear complex which may be considered as a structurally similar higher oligomer of the previously characterized linear μ-oxo-bridged binuclear complex $\{[MoO(TPP)]_2O\}$.

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Supporting Information Available: Tables S1−S18 giving complete crystallographic details, atomic coordinates, complete listings of bond distances and angles, anisotropic temperature factors, and fixed hydrogen atom positions for all complexes. An X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) EPR spectra for $[Mo_3O_4(TPP)_3]^+$ suggest at most a weak interaction between Mo centers. This is consistent with that previously seen for $\{[MoO(TPP)]_2O\}$ in a single crystal experiment.[26]

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