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Molecular Stereochemistry of Two Binuclear Metalloporphyrins Containing the $M_2O_3^{4+}$ Unit. μ-Oxo-bis(oxo-α,β,γ,δ-tetraphenylporphinatomolybdenum(V)) and Tri-μ-oxo-bis(α,β,γ,δ-tetraphenylporphinatoniobium(V))[1]

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The molecular stereochemistry of two binuclear metalloporphyrins with molecular formula $[O_3M_2(TPP)_2]$, where M = Nb(V) or Mo(V) and TPP is the dianion of α,β,γ,δ-tetraphenylporphyrin, have been determined by x-ray diffraction techniques using counter data. Crystal data: $O_3Nb_2(TPP)_2$, monoclinic, space group *Cc*, $Z = 4$, $a = 10.765$ (5) Å, $b = 24.913$ (6) Å, $c = 29.332$ (8) Å, $\cos\beta = -0.3794$ (4); $O_3Mo_2(TPP)_2$, monoclinic, space group *C*2/*c*, $Z = 4$, $a = 18.211$ (2) Å, $b = 19.309$ (3) Å, $c = 28.989$ (3) Å, $\cos\beta = -0.4320$ (1). Refinement of the niobium complex was based on 5748 observed data, final discrepancy indices $R_1 = 0.063$ and $R_2 = 0.073$. Refinement of the molybdenum complex was based on 7742 observed data, final discrepancy indices $R_1 = 0.059$ and $R_2 = 0.089$. The niobium complex is seven-coordinate with three bridging oxygen ligands. Unique Nb–O distances are 1.910, 1.990, 1.760, 1.782, 2.278, and 2.440 Å. The average Nb–N bond distance is 2.246 Å. The Nb–Nb separation is 2.872 Å. The molybdenum complex is six-coordinate; the $Mo_2O_3^{4+}$ unit has the unusual geometry of a linear five-atom grouping with two terminal Mo═O groups and a single Mo—O—Mo bridge. The Mo—O distances are 1.707 and 1.936 Å. This unusual arrangement for a binuclear Mo(V) complex leads to a paramagnetic species. The average Mo—N bond distance is 2.094 Å.

The early transition element metalloporphyrin derivatives frequently have as axial ligand(s) strongly bound oxygen atom(s) and form both mononuclear and binuclear complexes. Oxometalloporphyrin derivatives of niobium(V), tungsten(V), rhenium(V), and molybdenum(V) have been report by Buchler and co-workers.[2,3] Molybdenum(V) derivatives were first reported by Fleischer.[4] Niobium(V) derivatives have also been recently reported by Guilard et al.[5] One class of derivatives for all these metal ions has empirical formula $O_3M_2(P)_2$ where P is either the dianion of octaethylporphyrin or tetraphenylporphyrin. We have determined the molecular structure of two such derivatives where M is either niobium(V) or

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Table I. Summary of Crystal Data and Intensity Collection

Crystal	$O_3Mo_2(TPP)_2$	$O_3Nb_2(TPP)_2$
a, Å	18.211 (2)	10.765 (5)
b, Å	19.309 (3)	24.913 (6)
c, Å	28.989 (3)	29.332 (8)
cos β	−0.4320 (1)	−0.3794 (4)
Volume, Å^3	9193.7	7277.8
Calcd density, g/cm^3	1.47	1.43
Exptl density, g/cm^3	1.42	1.44
Cell content	$4[Mo_2O_3N_8C_{88}H_{56}\cdot C_8H_{10}\cdot 4CHCl_3]$	$4[Nb_2O_3N_8C_{88}H_{56}\cdot CHCl_3]$
Radiation	Graphite-monochromated Mo Kα (λ 0.710 69 Å)	
μ, mm^{-1}	0.595	0.467
Scan range	±0.25° from calcd peak position	±0.18° from calcd peak position
ω scan rate	0.5–8.0° min^{-1}	0.5 to 6.0° min^{-1}
Background	0.5 times scan time at scan extremes	1.0 times scan time at scan extremes
Background count displacement	±0.6°	±0.5°
Max (sin θ)/λ	$\leqslant$0.649	$\leqslant$0.690
Criterion for observn	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
Unique obsd data	7742	5748
Crystal dimensions, mm	0.4 × 0.4 × 0.5	0.2 × 0.2 × 0.5
Space group	$C2/c$	Cc

molybdenum(V) and P is the tetraphenylporphyrin dianion. These two derivatives have remarkably different molecular structures. The molybdenum(V) complex has a nearly linear O=MoOMo=O grouping and appears to be the prototype for most other derivatives with this empirical formula. The niobium(V) derivative, however, utilizes all three oxo ligands as bridging ligands between the two NbTPP units. We report herein the complete details of their molecular structures.[1]

Experimental Section

The compounds $O_3Mo_2(TPP)_2$ and $O_3Nb_2(TPP)_2$ were prepared following the procedures given by Rohbock[6] for the analogous octaethylporphyrin complexes. Crystals of $O_3Nb_2(TPP)_2$, suitable for x-ray study, were grown by diffusing methanol into a nearly saturated chloroform solution of the complex. Crystals of $O_3Mo_2(TPP)_2$ were obtained by adding a small amount of m-xylene to a nearly saturated chloroform solution of the complex and then adding a small volume of 10% aqueous ammonia and allowing the solution to slowly evaporate.[7]

Infrared spectra for the two complexes were recorded on a Perkin-Elmer 457 using KBr pellets. The niobium complex has no features in the 900–950-cm^{-1} region that could be associated with an Nb=O stretch. There is a medium-strong absorption at 515 cm^{-1} which appears to be associated with the Nb—O bonding system. The molybdenum complex shows a weak band at 905 cm^{-1}, which is probably an Mo=O stretch, and two bands at 615 and 565 cm^{-1}, which are presumed to be associated with the stretch in the Mo—O—Mo group.[8] The magnetic susceptibility of $O_3Mo_2(TPP)_2$ was measured on a Cahn Faraday balance at room temperature and was 1.7 μ_B per Mo atom.

Preliminary photographic examination of crystals of both compounds established four-molecule monoclinic unit cells. The lattice constants of the two compounds, listed in Table I, came from the least-squares refinement of the setting angles of 30 reflections, each collected at $\pm 2\theta$, at the ambient laboratory temperature of 20 ± 1 °C. X-ray intensity data were collected using graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer with "wandering" ω-scan techniques using programs and conditions as described previously.[9] Additional details are given in Table I. Five standard reflections for the Mo complex and four standard reflections for the Nb crystal, which were well distributed in reciprocal space, were measured periodically during data collection. The crystals of the Mo complex showed a small (~2%) decline in the values of the standard reflections; no such decline was observed with the Nb complex. Intensity data were reduced to a set of relative squared amplitudes as described previously;[10] no correction for absorption was deemed necessary. The total number of unique observed reflections for the two crystals is listed in Table I.

The systematic extinctions displayed by both crystals lead to the choice of Cc or $C2/c$ as the space group. Assuming that the complexes are binuclear species, the choice of $C2/c$ as the space group demands that the complex possess a crystallographic symmetry element. This is either a center of symmetry or a twofold axis of symmetry. Only the twofold axis of symmetry is a reasonable choice and its probable location would be through a bridging oxygen ligand with the porphinato planes of the complex approximately parallel to the twofold axis. This leads to the requirement that the y coordinate of the two metal atoms in the binuclear complex have the same value. On the other hand, the space group Cc requires no symmetry for the binuclear complex. The Patterson function for the Mo complex is consistent with the presence of a required twofold axis of symmetry and the space group $C2/c$ was assumed. This choice was confirmed by all subsequent developments during structure analysis. The Patterson function for the Nb complex, however, was not consistent with the presence of a twofold axis of symmetry but rather two independent niobium atom positions. The space group Cc was therefore chosen and all subsequent developments of the structure analysis of the niobium complex were consistent with this choice.

The structure of the Mo complex was obtained by the usual heavy-atom method.[11] In the later stages of structure solution, it was found that one of the two independent $CHCl_3$ molecule sites was partially occupied, as evidenced by comparative Fourier peaks and the experimental density. This was approximated by assigning occupancy factors of 0.5 for all atoms of this $CHCl_3$ molecule. The m-xylene molecule is located at an inversion center at $^1/_4$, $^1/_4$, 0; the methyl groups are disordered over two sites. The structure was refined by block-diagonal least-squares techniques.[12] Difference Fourier syntheses led to the placement of all hydrogen atoms in the molecule; the coordinates of the hydrogen atoms were idealized (C–H = 0.95 Å, $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$ Å^2) and included in subsequent refinement cycles as fixed contributors. Refinement was continued to convergence using anisotropic temperature factors for all heavy atoms. The final value of $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.057 and that of $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2}$ was 0.089; the estimated standard deviation of an observation of unit weight was 3.08. A final difference Fourier had no peaks larger than 0.60 e/Å^3; the largest peaks were in the region near the chloroform solvent molecules. A final listing of observed and calculated structure amplitudes is available as supplementary material.

The structure of the Nb complex was also solved by the heavy-atom method. The structure requires defining the coordinates of the 105 atoms in the asymmetric unit of structure; the origin of the cell was defined by fixing the x and z coordinates of Nb_1. Refinement of structure used block-diagonal least-squares methods[12] with the final cycles having anisotropic temperature factors for the 13 atoms of the coordination group and the 3 chlorine atoms of the $CHCl_3$ solvate. The final value of R_1 was 0.0625 and $R_2 = 0.0733$ with the estimated standard deviation of an observation of unit weight of 1.46.

Although a final difference Fourier map provided evidence for the positions of many hydrogen atoms of the molecule, these were not included in the refinement owing to the large size of the structure. A final listing of observed and calculated structure factors is available; see supplementary material.

The final atomic coordinates with equivalent isotropic thermal parameters and the associated anisotropic temperature factors in the asymmetric unit of structure in $O_3Mo_2(TPP)_2$ are listed in Tables II and III, respectively. The corresponding data for the atoms in the asymmetric unit of structure of $O_3Nb_2(TPP)_2$ are listed in Tables IV and V. (Tables III and V are available as supplementary material.)

Results and Discussion

The $O_3Nb_2(TPP)_2$ Molecule. Figure 1 provides a model in perspective[13] of the $O_3Nb_2(TPP)_2$ molecule in which the phenyl rings have been omitted for the sake of clarity. The molecule clearly utilizes the three oxo ligands as bridges between the two NbTPP moieties. Figures 2 and 3 provide "dissected" views of the molecule, with Figure 2 showing the porphinato ligand and the oxo ligands as they are associated with Nb_1 and Figure 3 the ligands associated with Nb_2. Together, the two

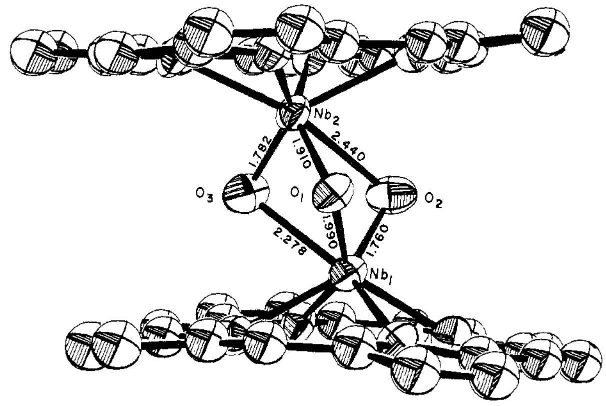

Figure 1. A model in perspective of the $O_3Nb_2(TPP)_2$ molecule. The peripheral phenyl rings have been omitted for clarity.

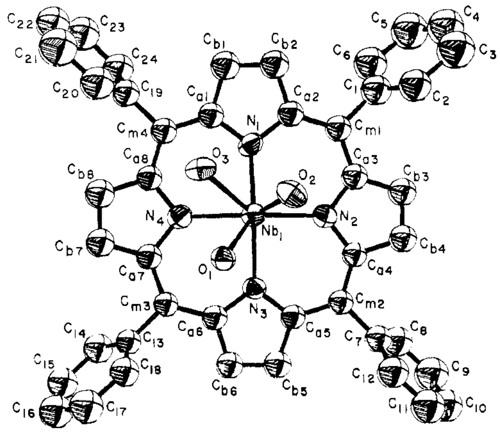

Figure 2. A view of the porphinato ligand and the oxo ligands coordinated to Nb_1. The porphinato plane and the paper are coplanar. The labeling scheme for all atoms in this half of the molecule is shown.

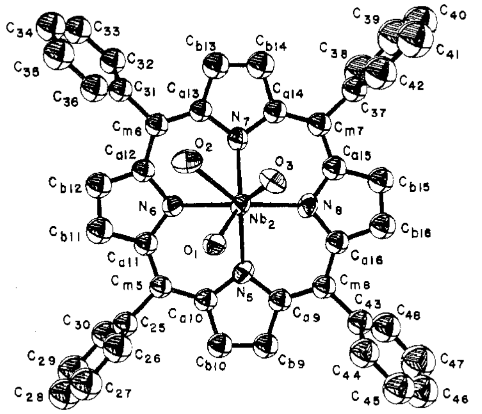

Figure 3. A view of the porphinato ligand and the oxo ligands associated with Nb_2. The porphinato plane and the paper are coplanar. The labeling scheme for the atoms is displayed.

figures also display the labeling scheme used for the atoms in the complete molecule. In each of these figures, the plane of the paper and the mean porphinato plane are coplanar. The stereochemical parameters of the 13-atom $N_4NbO_3NbN_4$ molecular core are listed in Table VI. Bond lengths in the porphinato ligands are listed in Table VII and bond angles in Table VIII (supplementary material).

Table II. Atomic Coordinates and Isotropic Thermal Parameters in the Unit Cell ($O_3Mo_2(TPP)_2$)

Atom type	Coordinates[a] 10^4x	10^4y	10^4z	B,[b] Å^2
Mo[c]	1176 (0)	2507 (0)	2773 (0)	2.44
O_1	0	2519 (2)	1/4	2.7
O_2	2211 (2)	2468 (1)	3014 (1)	3.8
N_1	1048 (2)	2795 (2)	2046 (1)	2.7
N_2	1082 (2)	1463 (1)	2563 (1)	2.7
N_3	1188 (2)	2220 (2)	3474 (1)	2.8
N_4	1176 (2)	3556 (2)	2959 (1)	2.9
C_{a1}	1136 (2)	3458 (2)	1904 (1)	3.0
C_{a2}	1084 (2)	2338 (2)	1692 (1)	3.0
C_{a3}	1025 (2)	1217 (2)	2107 (1)	3.0
C_{a4}	1103 (2)	909 (2)	2873 (1)	3.0
C_{a5}	1309 (2)	1560 (2)	3660 (1)	3.0
C_{a6}	1309 (2)	2684 (2)	3867 (1)	2.9
C_{a7}	1169 (2)	3799 (2)	3399 (1)	2.8
C_{a8}	1122 (2)	4109 (2)	2644 (1)	2.8
C_{b1}	1234 (3)	3411 (2)	1438 (1)	3.4
C_{b2}	1212 (3)	2740 (2)	1315 (1)	3.4
C_{b3}	962 (2)	471 (2)	2117 (1)	3.4
C_{b4}	999 (2)	288 (2)	2574 (1)	3.3
C_{b5}	1531 (2)	1609 (2)	4206 (1)	3.5
C_{b6}	1521 (3)	2274 (2)	4323 (1)	3.3
C_{b7}	1085 (2)	4538 (2)	3352 (1)	3.3
C_{b8}	1052 (2)	4721 (2)	2895 (1)	3.3
C_{m1}	1051 (2)	1615 (2)	1713 (1)	3.0
C_{m2}	1242 (2)	949 (2)	3380 (1)	3.1
C_{m3}	1260 (2)	3395 (2)	3826 (1)	2.9
C_{m4}	1141 (2)	4067 (2)	2171 (1)	2.8
C_1	1107 (2)	1234 (2)	1281 (1)	3.2
C_2	489 (3)	1261 (2)	787 (1)	4.0
C_3	585 (3)	904 (3)	391 (2)	5.0
C_4	1267 (3)	532 (3)	491 (2)	5.0
C_5	1866 (3)	509 (3)	964 (2)	5.2
C_6	1801 (3)	858 (2)	1369 (2)	4.2
C_7	1347 (2)	280 (2)	3659 (1)	3.2
C_8	840 (2)	99 (2)	3883 (1)	3.7
C_9	904 (3)	−532 (2)	4119 (2)	4.2
C_{10}	1507 (3)	−988 (2)	4147 (2)	4.9
C_{11}	2018 (3)	−821 (2)	3935 (2)	4.7
C_{12}	1948 (3)	−193 (2)	3695 (2)	4.0
C_{13}	1326 (2)	3784 (2)	4292 (1)	3.0
C_{14}	773 (3)	3659 (2)	4494 (1)	3.9
C_{15}	815 (3)	4027 (3)	4917 (2)	4.9
C_{16}	1394 (3)	4520 (3)	5131 (2)	4.9
C_{17}	1971 (3)	4646 (2)	4942 (2)	4.6
C_{18}	1925 (3)	4274 (2)	4521 (1)	3.7
C_{19}	1195 (2)	4732 (2)	1926 (1)	3.0
C_{20}	1826 (2)	5190 (2)	2175 (2)	3.9
C_{21}	1892 (3)	5799 (2)	1955 (2)	4.5
C_{22}	1315 (3)	5959 (2)	1465 (2)	4.6
C_{23}	681 (3)	5514 (2)	1211 (2)	4.6
C_{24}	623 (3)	4904 (2)	1435 (1)	3.7
C_{25}	1826 (5)	2728 (5)	38 (4)	10.3
C_{26}	2234 (5)	2229 (5)	357 (4)	10.3
C_{27}	2939 (6)	1977 (5)	328 (4)	11.6
C_{28}	3876 (11)	1840 (17)	18 (10)	15.2
C_{29}	3572 (13)	1467 (10)	721 (11)	14.4
C_{30}	3730 (4)	3026 (3)	3921 (3)	7.0
C_{31}	3320 (10)	2567 (10)	2425 (7)	10.2
Cl_1	3565 (2)	3919 (1)	3846 (1)	12.2
Cl_2	4700 (1)	2839 (1)	4030 (2)	12.5
Cl_3	3521 (2)	2709 (2)	4384 (1)	15.9
Cl_4	3376 (5)	3454 (4)	2460 (3)	17.9
Cl_5	3455 (7)	2407 (5)	1840 (5)	24.2
Cl_6	4174 (9)	2217 (8)	2753 (5)	30.0

[a] Numbers in parentheses are estimated standard deviations. [b] No estimated standard deviation given since thermal parameters were refined anisotropically. Isotropic thermal parameters are calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/2}$. [c] For Mo 10^5x = 11755 (2), 10^5y = 25069 (2), 10^5z = 27727 (1).

We consider first the coordination groups of the $O_3Nb_2(TPP)_2$ molecule. The eight individual Nb–N distances (Table VI) are essentially all equivalent with an average value of 2.246 Å. In contrast, the Nb–O distances of each unique niobium atom are seen to be significantly different. O_1 forms a nearly symmetric bridge between the two niobium atoms. On the other hand, O_2 and O_3 form quite asymmetric links with each oxygen closely associated with a different Nb atom

Table IV. Atomic Coordinates and Isotropic Thermal Parameters in the Unit Cell $(O_3Nb_2(TPP)_2)$

Atom type	Coordinates[a] 10^4x	10^4y	10^4z	B,[b] Å^2	Atom type	Coordinates[a] 10^4x	10^4y	10^4z	B,[b] Å^2
Nb_2[c]	980 (1)	−830 (0)	−718 (0)	3.09	C_{21}	−3002 (19)	−2713 (7)	−2193 (7)	9.1 (4)
Nb_1[c]	0	−1235 (0)	0	3.34	C_{22}	−3717 (15)	−3167 (6)	−2195 (5)	6.9 (3)
O_1	−4 (6)	−550 (2)	−349 (2)	3.5	C_{23}	−3890 (16)	−3300 (7)	−1781 (6)	7.6 (3)
O_2	1715 (7)	−1250 (3)	94 (3)	4.5	C_{24}	−3432 (13)	−2999 (5)	−1343 (5)	6.1 (3)
O_3	7 (7)	−1421 (3)	−759 (3)	4.2	C_{a9}	−681 (9)	118 (4)	−1470 (4)	3.8 (2)
N_1	−280 (8)	−2119 (3)	−75 (3)	3.8	C_{a10}	634 (9)	450 (4)	−751 (4)	3.9 (2)
N_2	806 (8)	−1472 (3)	798 (3)	3.9	C_{a11}	2639 (10)	158 (4)	−52 (4)	4.1 (2)
N_3	−1016 (7)	−654 (3)	332 (3)	3.5	C_{a12}	3908 (10)	−567 (4)	130 (4)	3.9 (2)
N_4	−2205 (8)	−1317 (3)	−525 (3)	3.8	C_{a13}	3869 (9)	−1430 (4)	−294 (4)	3.7 (2)
N_5	388 (7)	−11 (3)	−1042 (3)	3.6	C_{a14}	2574 (10)	−1747 (4)	−1022 (4)	4.1 (2)
N_6	2734 (7)	−357 (3)	−214 (3)	3.5	C_{a15}	584 (10)	−1444 (4)	−1721 (4)	4.3 (2)
N_7	2739 (8)	−1314 (3)	−712 (3)	3.7	C_{a16}	−746 (10)	−725 (4)	−1893 (4)	4.0 (2)
N_8	377 (8)	−962 (3)	−1530 (3)	3.6	C_{b9}	−1114 (11)	660 (4)	−1450 (4)	4.7 (2)
C_{a1}	−968 (10)	−2385 (4)	−506 (4)	4.1 (2)	C_{b10}	−295 (11)	865 (4)	−1007 (4)	4.5 (2)
C_{a2}	723 (10)	−2472 (4)	211 (4)	4.3 (2)	C_{b11}	3771 (12)	262 (5)	404 (4)	5.3 (2)
C_{a3}	1583 (10)	−1929 (4)	985 (4)	4.4 (2)	C_{b12}	4558 (11)	−185 (4)	509 (4)	5.0 (2)
C_{a4}	1087 (10)	−1140 (4)	1198 (4)	3.9 (2)	C_{b13}	4395 (12)	−1939 (5)	−350 (4)	5.3 (2)
C_{a5}	−509 (9)	−427 (4)	787 (4)	3.9 (2)	C_{b14}	3639 (12)	−2139 (5)	−792 (5)	5.6 (2)
C_{a6}	−2045 (10)	−318 (4)	50 (4)	4.2 (2)	C_{b15}	−395 (11)	−1520 (5)	−2210 (4)	4.9 (2)
C_{a7}	−3069 (10)	−882 (4)	−702 (4)	4.1 (2)	C_{b16}	−1231 (11)	−1078 (5)	−2314 (4)	5.0 (2)
C_{a8}	−2685 (10)	−1706 (4)	−891 (4)	4.1 (2)	C_{m5}	1636 (9)	516 (4)	−282 (3)	3.6 (2)
C_{b1}	−353 (12)	−2896 (5)	−513 (5)	5.4 (2)	C_{m6}	4396 (9)	−1091 (4)	106 (4)	3.9 (2)
C_{b2}	708 (11)	−2948 (5)	−73 (4)	5.2 (2)	C_{m7}	1594 (10)	−1816 (4)	−1484 (4)	4.2 (2)
C_{b3}	2347 (11)	−1864 (5)	1498 (4)	5.0 (2)	C_{m8}	−1269 (10)	−226 (4)	−1856 (4)	4.1 (2)
C_{b4}	2074 (11)	−1387 (4)	1629 (4)	4.9 (2)	C_{25}	1611 (10)	1039 (4)	−9 (4)	4.5 (2)
C_{b5}	−1214 (11)	56 (4)	796 (4)	4.8 (2)	C_{26}	638 (13)	1078 (5)	187 (5)	6.1 (3)
C_{b6}	−2157 (11)	125 (4)	346 (4)	4.7 (2)	C_{27}	516 (16)	1551 (6)	432 (6)	7.4 (3)
C_{b7}	−4079 (12)	−991 (5)	−1177 (4)	5.2 (2)	C_{28}	1390 (15)	1972 (6)	460 (6)	7.1 (3)
C_{b8}	−3899 (12)	−1515 (5)	−1293 (5)	5.6 (2)	C_{29}	2327 (16)	1940 (6)	259 (6)	7.4 (3)
C_{m1}	1572 (10)	−2388 (4)	694 (4)	4.3 (2)	C_{30}	2435 (13)	1443 (5)	8 (5)	5.8 (2)
C_{m2}	524 (10)	−638 (4)	1197 (4)	4.0 (2)	C_{31}	5509 (10)	−1304 (4)	553 (4)	4.0 (2)
C_{m3}	−2949 (9)	−398 (4)	−435 (4)	3.9 (2)	C_{32}	6774 (11)	−1410 (5)	564 (4)	5.0 (2)
C_{m4}	−2106 (10)	−2199 (4)	−886 (4)	4.4 (2)	C_{33}	7769 (13)	−1603 (5)	1009 (5)	5.8 (2)
C_1	2510 (13)	−2839 (5)	958 (5)	5.9 (3)	C_{34}	7443 (13)	−1696 (5)	1423 (5)	6.3 (3)
C_2	3855 (14)	−2752 (6)	1163 (5)	6.5 (3)	C_{35}	6181 (14)	−1601 (6)	1409 (5)	6.7 (3)
C_3	4735 (19)	−3211 (8)	1481 (7)	9.0 (4)	C_{36}	5180 (12)	−1390 (5)	972 (5)	5.4 (2)
C_4	4052 (18)	−3654 (7)	1508 (7)	8.6 (4)	C_{37}	1600 (11)	−2315 (4)	−1762 (4)	4.8 (2)
C_5	2787 (19)	−3755 (8)	1322 (7)	9.0 (4)	C_{38}	2480 (19)	−2360 (8)	−2000 (7)	9.1 (4)
C_6	1907 (15)	−3321 (6)	1003 (6)	7.3 (3)	C_{39}	2499 (22)	−2866 (9)	−2274 (8)	10.2 (5)
C_7	958 (11)	−336 (4)	1674 (4)	4.7 (2)	C_{40}	1625 (18)	−3255 (7)	−2280 (7)	8.7 (4)
C_8	617 (13)	−507 (6)	2062 (5)	6.3 (3)	C_{41}	708 (20)	−3219 (8)	−2038 (8)	9.7 (5)
C_9	1031 (17)	−225 (7)	2513 (6)	7.9 (4)	C_{42}	760 (16)	−2737 (7)	−1780 (6)	7.9 (4)
C_{10}	1738 (15)	234 (6)	2558 (6)	7.0 (3)	C_{43}	−2532 (11)	−44 (4)	−2270 (4)	4.7 (2)
C_{11}	2037 (16)	424 (6)	2187 (6)	7.4 (3)	C_{44}	−3682 (13)	54 (5)	−2180 (5)	6.1 (3)
C_{12}	1673 (14)	149 (6)	1732 (5)	6.3 (3)	C_{45}	−4846 (15)	256 (6)	−2590 (6)	7.3 (3)
C_{13}	−3898 (10)	33 (4)	−686 (4)	4.0 (2)	C_{46}	−4774 (17)	370 (7)	−3010 (6)	8.1 (4)
C_{14}	−5276 (12)	−18 (5)	−824 (5)	5.7 (2)	C_{47}	−3695 (19)	276 (8)	−3120 (7)	9.1 (4)
C_{15}	−6129 (13)	402 (5)	−1079 (5)	6.1 (3)	C_{48}	−2502 (14)	82 (6)	−2731 (5)	6.6 (3)
C_{16}	−5637 (15)	855 (6)	−1194 (6)	7.1 (3)	Cl_1	−5050 (8)	−2196 (3)	−3440 (3)	12.9
C_{17}	−4258 (16)	914 (6)	−1060 (6)	7.2 (3)	Cl_2	−5364 (14)	−1065 (3)	−3350 (5)	16.9
C_{18}	−3376 (12)	509 (5)	−791 (5)	5.4 (2)	Cl_3	−6126 (17)	−1797 (5)	−2782 (5)	18.9
C_{19}	−2662 (11)	−2540 (4)	−1335 (4)	4.6 (2)	C_{49}	−6011 (28)	−1699 (12)	−3359 (11)	13.4 (7)
C_{20}	−2439 (15)	−2398 (6)	−1750 (5)	6.8 (3)					

[a] Numbers in parentheses are the estimated standard deviations. [b] Thermal parameters for which no estimated standard deviation is given were refined anisotropically. Isotropic thermal parameters are calculated from $B = 4[V^2\det(\beta_{ij})]^{1/2}$. [c] For Nb_2 $10^5x = 9797$ (10), $10^5y = -8305$ (3), $10^5z = -7176$ (4); for Nb_1 $10^5y = -12349$ (3).

(see Figure 1). Each niobium atom thus forms, with the three oxo ligands, one short, one long, and one intermediate-length Nb—O bond. The short Nb—O bonds, with individual values of 1.760 (7) and 1.782 (7) Å, are slightly longer than the Nb—O distances in complexes where this bond can be regarded as an isolated Nb═O double bond. The distances in complexes[14,15] with an Nb═O group range from 1.70 (6) Å[15a] in six-coordinate $[Nb(O)(NCS)_5]^{2-}$ to 1.74 (1) Å[15b] in seven-coordinate $Nb(O)(S_2CNEt_2)_3$. The other Nb—O bonds formed by these two oxo ligands are the long distances, with respective values of 2.440 (8) and 2.278 (7) Å. It is interesting to note that the longer of the two long Nb—O distances is paired with the shorter of the two short Nb—O distances and vice versa (cf. Figure 1). These long Nb—O distances are the longest such bonds observed, although Nb—O distances of up to 2.20 (2) Å are observed in eight-coordinate $Nb(O_2CNMe_2)_5$[16] and Nb—O distances of 2.223 (6) and 2.225 (6) Å are found in seven-coordinate $Nb(TPP)(O)(O_2CCH_3)$.[14] The symmetrically bridging oxo ligand, O_1, forms Nb—O bonds of length 1.910 (6) and 1.990 (6) Å. These are in the range of distances observed previously: 1.88 (1) Å in $\{[(\pi-C_5H_5)_2NbCl]_2O\}(BF_4)_2$[17] and 1.99 (1) Å in polymeric $NbOCl_3$.[18]

The coordination polyhedron around each niobium atom is of the 4 + 3 type with a square-planar base provided by the four porphinato nitrogen atoms and the trigonal-planar cap provided by the three oxo ligands. The planes defined by the base and cap are almost parallel. The dihedral angle between

Table VI. Stereochemical Parameters of the Coordination Group of the $O_3Nb_2(TPP)_2$ Molecule[a]

	Distances, Å		
Nb_1-O_1	1.990 (6)	$O_1\cdots O_2$	2.515 (9)
Nb_1-O_2	1.760 (7)	$O_2\cdots O_3$	2.515 (11)
Nb_1-O_3	2.278 (7)	$O_3\cdots O_1$	2.483 (9)
Nb_2-O_1	1.910 (6)	$O_1\cdots N_4$	2.934 (10)
Nb_2-O_2	2.440 (8)	$O_1\cdots N_6$	2.860 (10)
Nb_2-O_3	1.782 (7)	$O_1\cdots N_3$	2.629 (10)
Nb_1-N_1	2.222 (7)	$O_1\cdots N_5$	2.600 (10)
Nb_1-N_2	2.243 (8)	$O_2\cdots N_7$	2.97 (1)
Nb_1-N_3	2.248 (7)	$O_2\cdots N_1$	2.96 (1)
Nb_1-N_4	2.295 (8)	$O_2\cdots N_6$	2.78 (1)
Nb_2-N_5	2.240 (8)	$O_2\cdots N_2$	2.66 (1)
Nb_2-N_6	2.239 (7)	$O_3\cdots N_7$	2.90 (1)
Nb_2-N_7	2.239 (8)	$O_3\cdots N_1$	2.76 (1)
Nb_2-N_8	2.242 (7)	$O_3\cdots N_4$	2.73 (1)
$Nb_1\cdots Nb_2$	2.872 (1)	$O_3\cdots N_8$	2.69 (1)
	Angles, deg		
$N_1Nb_1N_2$	80.0 (3)	$O_2Nb_2N_6$	72.7 (3)
$N_2Nb_1N_3$	77.1 (3)	$O_2Nb_2N_7$	78.7 (3)
$N_3Nb_1N_4$	78.4 (3)	$O_3Nb_2N_7$	91.7 (3)
$N_4Nb_1N_1$	77.2 (3)	$O_3Nb_2N_8$	83.2 (3)
$N_5Nb_2N_6$	80.4 (3)	$O_1Nb_1O_2$	84.0 (3)
$N_6Nb_2N_7$	77.3 (3)	$O_2Nb_1O_3$	75.9 (3)
$N_7Nb_2N_8$	80.3 (3)	$O_3Nb_1O_1$	70.8 (2)
$N_8Nb_2N_5$	76.1 (3)	$O_1Nb_2O_2$	69.4 (2)
$O_1Nb_1N_3$	76.4 (3)	$O_2Nb_2O_3$	71.2 (3)
$O_1Nb_1N_4$	86.1 (3)	$O_3Nb_2O_1$	84.5 (3)
$O_2Nb_1N_1$	95.1 (3)	$Nb_1O_1Nb_2$	94.8 (3)
$O_2Nb_1N_2$	82.2 (3)	$Nb_1O_2Nb_2$	84.6 (3)
$O_3Nb_1N_1$	75.7 (3)	$Nb_1O_3Nb_2$	89.2 (3)
$O_3Nb_1N_4$	73.4 (3)	$N_1Nb_1N_3$	127.6 (3)
$O_1Nb_2N_5$	77.2 (3)	$N_2Nb_1N_4$	124.5 (3)
$O_1Nb_2N_6$	86.8 (3)	$N_5Nb_2N_7$	126.6 (3)
		$N_6Nb_2N_8$	127.5 (3)

[a] Figures in parentheses are estimated standard deviations.

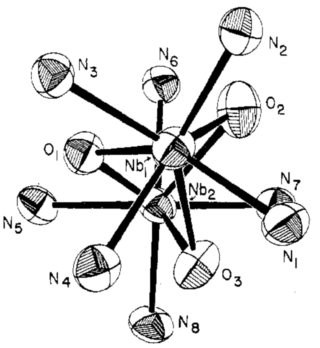

Figure 4. A drawing of the molecular core of the $O_3Nb_2(TPP)_2$ molecule. The three ligand planes of the molecule are parallel to the plane of the drawing.

the two planes around Nb_1 is 1.5° and that around Nb_2 is 3.3°. Nb_1 is displaced 1.34 Å from the oxygen plane and 1.02 Å from the plane of the four porphinato nitrogen atoms. The displacement values for Nb_2 are similar at 1.35 and 1.00 Å, respectively. The idealized symmetry of the coordination polyhedron of both niobium atoms is that of C_s (cf. Figures 2 and 3). Note that for both coordination polyhedra, the long Nb–O bond lies in the mirror plane.[19] The same coordination polyhedron, with similar out-of-plane displacements, is observed in seven-coordinate oxoacetato-α,β,γ,δ-tetraphenylporphinatoniobium(V).[14]

As can be seen from Figures 1 and 4, the two porphinato rings have a "slipped" configuration with respect to each other; the angles between the normals to the ring passing through the closest niobium atom and the Nb–Nb vector are 18 and 21°. The important effect of this feature appears to be that the three planes of ligand atoms can thus remain approximately parallel to each other. The dihedral angle between the two nitrogen atom planes is only 3.6°. The slipped arrangement of the two porphinato rings appears not to be required by inter-ring contacts; the interplanar spacing between the two 24-atom porphinato cores is ~4.9 Å.

Table IX. Averaged Values for Bond Angles (deg) and Distances (Å) in Respective Porphinato Ligands[a,b]

Bond angles	$O_3Nb_2(TPP)_2$[c]	$O_3Mo_2(TPP)_2$
C_aNC_a	105.4 (6)	109.2 (3)
NC_aC_b	110.1 (7)	107.1 (4)
NC_aC_m	125.4 (13)	126.0 (3)
$C_aC_bC_b$	107.1 (7)	108.2 (3)
$C_aC_mC_a$	124.5 (9)	126.8 (5)
Bond distances	$O_3Nb_2(TPP)_2$	$O_3Mo_2(TPP)_2$
M-N	2.246 (21)	2.094 (3)
N-C_a	1.385 (12)	1.376 (10)
C_a-C_m	1.391 (18)	1.396 (12)
C_a-C_b	1.439 (12)	1.441 (10)
C_b-C_b	1.355 (23)	1.341 (8)

[a] The figure in parentheses is the estimated standard deviation of the average. [b] C_a and C_b represent the respective α- and β-carbon atoms of a pyrrole ring and C_m methine carbon atoms. [c] Values listed for $O_3Nb_2(TPP)_2$ are averaged over both porphinato ligands of the molecule.

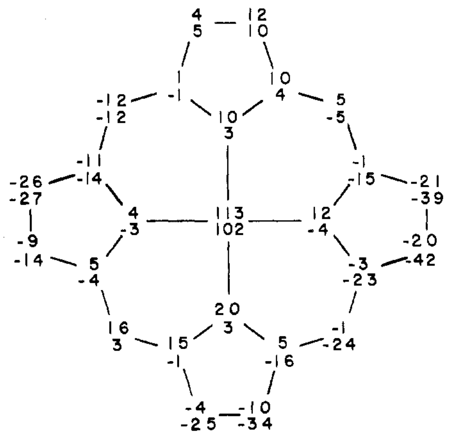

Figure 5. A formal diagram of the porphinato skeleton associated with Nb_1. The orientation of the skeleton is the same as that shown in Figure 2. The upper value of the pair of values is the perpendicular displacement, in units of 0.01 Å, from the mean plane of the 24-atom core. The lower values are the perpendicular displacements from the mean plane of the four porphinato nitrogen atoms. The dihedral angle between these two planes is 1.9°.

The idealized symmetry of the 13-atom core of the binuclear complex is C_2. The idealized twofold axis passes through O_1 and is parallel to the two porphinato planes. Indeed, we subsequently obtained crystals of $O_3Nb_2(TPP)_2$, as an unsolvated crystal, in which this molecular symmetry element is crystallographically demanded.[20] Lecomte and co-workers[21] have also reported, in a preliminary communication, the structure of a third polymorph of $O_3Nb_2(TPP)_2$ in which the binuclear complex has required C_2 symmetry. The idealized symmetry of the coordination polyhedron of an individual niobium atom is similar to those reported here. However, there are significant differences in their Nb–O distances and ours. They report 1.89 (2) Å for the symmetrically bridging bond distances and 1.83 (3) and 1.94 (3) Å for the distances that correspond to our short and long distances. These differences, if correct, suggest considerable flexibility in the tri-μ-oxo bridging system.

Averaged values for chemically equivalent bond types in the two porphinato cores are given in Table IX. The individual C–C bond distances in the eight structurally independent phenyl rings average to 1.39 (5) Å. The dihedral angles between the phenyl rings and the plane of the appropriate

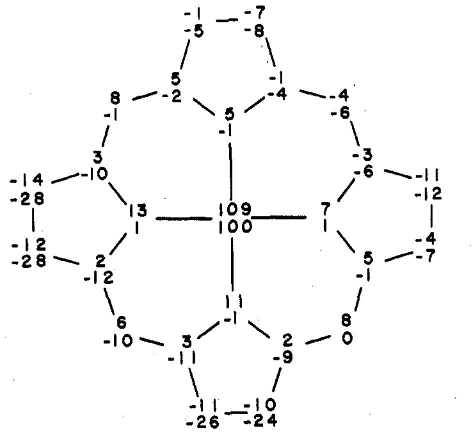

Figure 6. A formal diagram of the porphinato skeleton of Nb_2. The orientation of the figure is the same as that of Figure 3. The upper value of the pair of values is the perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core. The lower value is the perpendicular displacement from the mean plane of the porphinato nitrogen atoms. The dihedral angle between the mean planes is 1.2°.

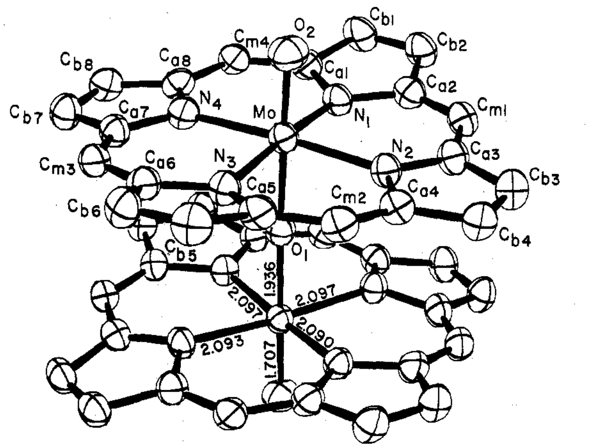

Figure 7. A computer-drawn model of the $O_3Mo_2(TPP)_2$ molecule. The phenyl rings are not shown to improve visibility. The labels for the unique atoms of the core are shown. Also displayed are the values of bond distances in the coordination group of the molecule.

porphinato core are 59.8, 71.5, 68.0, 71.3, 76.6, 67.6, 79.3, and 65.5°.

Figures 5 and 6 display some aspects of the conformation of the two independent porphinato cores of the molecule. These figures are drawn with the same general orientation as Figures 2 and 3, respectively. Each labeled atom of Figures 2 and 3 has been replaced by the value of the perpendicular displacements, in units of 0.01 Å, from the mean plane of the 24-atom core (top value) and from the mean plane of the four porphinato nitrogen atoms (bottom value) in Figures 5 and 6. The simplest description of the two cores can be given by noting their similarity to the three sides and raised flap of an umbrella tent in which the sides and flap are composed of individual pyrrole rings. Similar conformations of the porphinato core are seen in Tl(OEP)(Cl)[22] and Mn(TPP)(1-MeIm).[23] Figures 5 and 6 also show that, to a very crude approximation, the entire core "domes" away from the nitrogen atom plane by ~0.1 Å. These features appear to reflect an accommodation of the porphinato core to being coordinated to a very large metal atom. As is usual, individual units of the tetraphenylporphinato ligands retain planarity.

The molecules are well separated in the crystal. Closest nonbonded contacts are between phenyl carbon atoms of adjacent molecules and range from 3.5 Å upward. One contact between the solvent molecule and a phenyl carbon atom is 3.4 Å; all others are greater than 3.7 Å.

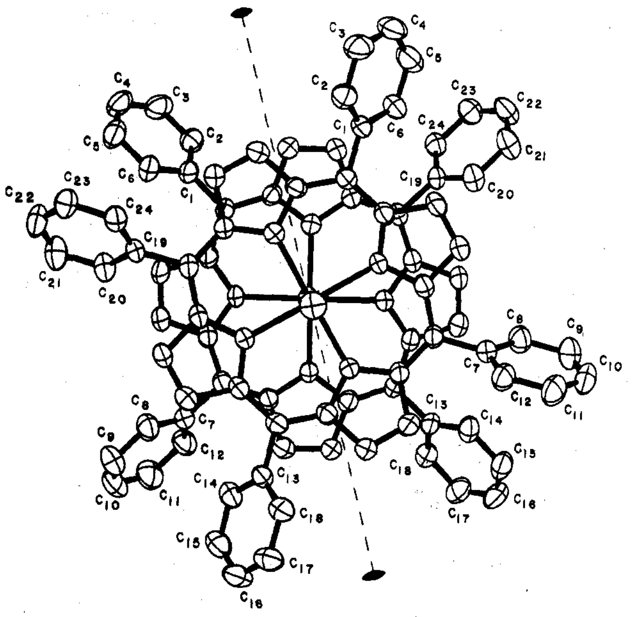

Figure 8. A drawing of the entire $O_3Mo_2(TPP)_2$ molecule viewed down the Mo–O–Mo axis. The required twofold axis, which passes through the bridging oxo oxygen atom, requires structural equivalence of the upper and lower halves of the binuclear complex.

Table X. Stereochemical Parameters of the Coordination Group of the $O_3Mo_2(TPP)_2$ Molecule[a]

	Distances, Å		
Mo-O_1	1.936 (3)	$O_1\cdots N_2$	2.785 (3)
Mo-O_2	1.707 (3)	$O_1\cdots N_3$	2.778 (3)
Mo-N_1	2.093 (3)	$O_1\cdots N_4$	2.813 (3)
Mo-N_2	2.090 (3)	$O_2\cdots N_1$	2.763 (4)
Mo-N_3	2.097 (3)	$O_2\cdots N_2$	2.717 (4)
Mo-N_4	2.097 (3)	$O_2\cdots N_3$	2.760 (4)
$O_1\cdots N_1$	2.797 (4)	$O_2\cdots N_4$	2.782 (4)
	Angles, deg		
N_1MoN_2	90.2 (1)	O_1MoN_4	88.4 (1)
N_2MoN_3	89.5 (1)	O_2MoN_1	92.7 (1)
N_3MoN_4	90.4 (1)	O_2MoN_2	90.8 (1)
N_4MoN_1	89.4 (1)	O_2MoN_3	92.4 (1)
O_1MoN_1	87.9 (1)	O_2MoN_4	93.4 (1)
O_1MoN_2	87.5 (1)	O_1MoO_2	178.2 (2)
O_1MoN_3	87.0 (1)	N_1MoN_3	174.8 (1)
		N_2MoN_4	175.8 (1)

[a] Figures in parentheses are estimated standard deviations.

The $O_3Mo_3(TPP)_2$ Molecule. Figure 7 is a view of the $O_3Mo_2(TPP)_2$ in which the phenyl rings have been omitted for clarity. The figure also displays the labeling scheme for the unique atoms of a porphinato core. Figure 8 gives a view of the entire molecule with the position of the crystallographically required twofold axis also shown. Table X lists the stereochemical parameters of the coordination group. Individual bond lengths in the porphinato ligand are tabulated in Table XI and bond angles are given in Table XII (supplementary material).

Oxo-bridged molybdenum(V) complexes which also contain terminal Mo=O units are rather common; however, the configuration observed in $O_3Mo_2(TPP)_2$ is unique among structurally characterized Mo(V) complexes.[24] As is seen in Figures 7 and 8, the terminal oxo groups are trans to the bridging oxo ligand with the O=Mo—O angle equal to 178.2 (2)°. Other binuclear Mo(V) complexes have the terminal Mo=O units cis to the bridging oxo ligand. The paramagnetism of $O_3Mo_2(TPP)_2$,[2,4,25] as contrasted to the diamagnetism of other binuclear Mo(V) complexes, results from this trans arrangement of the oxo ligands. The terminal Mo=O group fixes the *z* direction and each Mo(V) atom almost surely has the ground state $(4d_{xy})^1$.[24,26] The observed configuration in $O_3Mo_2(TPP)_2$ thus inhibits overlap of the $4d_{xy}$ orbitals on the two Mo(V) atoms.

The terminal Mo═O bond distance is 1.708 (3) Å and the bridging Mo—O bond distance is 1.936 (3) Å. The terminal bond distance is 0.02–0.05 Å longer than the normal length[27,28] and the bridging distance is ~0.10 Å longer than the usual distance observed in other $Mo_2O_3^{4+}$ binuclear complexes.[26,28] The lengthening of the two types of bonds is presumably the result of the mutual trans influence of the oxo ligands. The five atom O═MoOMo═O group is nearly linear with an O_2MoO_1 bond angle of 178.2 (2)° and an MoO_1Mo' bond angle of 178.63 (6)°. The Mo(V) atom is displaced 0.09 Å out of the plane defined by the four porphinato nitrogen atoms toward the terminal oxo ligand and not on the bridge side of the plane. This small displacement of the molybdenum atom (assuming constant Mo—O distances) leads to near-equalization of the O···N packing contacts (see Table X); the O_1···N distances average to 2.79 Å and the O_2···N distances to 2.76 Å.

The average Mo—N bond distance of 2.094 (3) Å compares well with the 2.096 (4) Å value found in a molybdenum(VI) porphyrin.[29]

An examination of Figure 8 shows that the upper and lower porphinato skeletons are in a staggered configuration that roughly corresponds to D_{4d} symmetry for the molecule as a whole. For exact D_{4d} symmetry, the angle of twisting the upper skeleton about the true $\bar{8}$ axis from exact superposition with the lower skeleton would be 45°; the observed twist angle is 59.6°. Similar orientations of the two porphinato skeletons are observed in two other binuclear metalloporphyrins; the twist angle in $(FeTPP)_2O$[30] is 54.6° and in $(FeTPP)_2N$[31] the twist angle is 58.3°. The dominant feature which leads to these similar twist angles may be the inter-ring, intramolecular phenyl–porphinato core contacts. These three derivatives form a series of complexes with decreasing porphyrin interplanar spacings: ~4.25 Å in $(FeTPP)_2O$,[30] ~4.15 Å in $(FeTPP)_2N$,[31] and ~3.85 Å in $O_3Mo_2(TPP)_2$. The approach of the two porphinato cores is hindered by the packing of the bulky phenyl substituents as is easily observed from molecular models. Closer approach of the two cores is achieved by flattening the overall molecule and thus the dihedral angles between the porphinato core and the phenyl substituents become increasingly smaller as the two porphinato planes approach. This is clearly seen in the unique dihedral angles between the phenyl groups and the porphinato core of the three derivatives. The unique dihedral angles in $(FeTPP)_2O$[30] are 82.8, 82.7, 77.0, and 53.3° and in $(FeTPP)_2N$[31] are 54.0 and 65.4°. In $O_3Mo_2(TPP)_2$, all phenyl dihedral angles are quite small at 53.6, 64.0, 53.8, and 54.2°. In $O_3Mo_2(TPP)_2$, intramolecular phenyl hydrogen atom to β-pyrrole carbon atom nonbonded distances range from 2.80 Å upward and would be shorter were the dihedral angles to be closer to 90°.

Averaged values for chemically equivalent bond distances and angles in the porphinato ligand of $O_3Mo_2(TPP)_2$ are given in Table IX. The average of the 24 individually determined C–C bond distances in the peripheral phenyl rings is 1.35 (2) Å. Figure 9 is a formal diagram of the porphinato core showing atom displacements from two mean planes. The figure is drawn with the same general orientation as Figure 7. Each labeled atom of Figure 7 has been replaced by the value of the perpendicular displacements, in units of 0.01 Å, from the mean plane of the 24-atom core (top value) and from the mean plane of the four porphinato nitrogen atoms (bottom value) in Figure 9. A plus value represents a displacement on the bridging oxo ligand side of the porphinato plane. The displacement of atoms in the core conforms closely to D_{2d} symmetry. This type of quasi-D_{2d} ruffling of the core has been noted and discussed previously.[9] There are no unusual nonbonded contacts between molecules in the crystal.

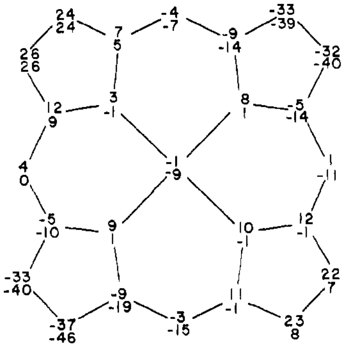

Figure 9. A formal diagram of the unique porphinato skeleton in $O_3Mo_2(TPP)_2$. The orientation is the same as in Figure 7. The upper value of the pair of values is the perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core. The lower value of the pair of values is the displacement from the mean plane of the porphinato nitrogen atoms. The dihedral angle between the two planes is 1.0°.

Comparison and Summary of the Two Structures. It may be noted that the averaged values of bond parameters in the respective porphinato cores of the two molecules (Table IX) differ significantly. These differing values, however, are consonant with the differing sizes of the central hole of the cores.[32] With the Mo(V) atom almost centered in the porphinato ligand, the core in $O_3Mo_2(TPP)_2$ is expanded to a Ct···N radius of 2.092 Å. In the $O_3Nb_2(TPP)_2$ molecule the radius of the central hole is 2.006 Å. The large displacement of the niobium atom allows the porphinato ligand to assume a central hole size consistent with minimum strain in the macrocycle.[33]

Given the close positions of niobium and molybdenum in the periodic table, a natural question is why the two compounds have such different structures. Based on the similarity in the infrared spectra, the rhenium(V) and tungsten(V) analogues appear to utilize the $O_3Mo_2(TPP)_2$ structure.[34] Thus among the four derivatives having empirical formula $O_3M_2(P)_2$, the niobium(V) complex is unique. The differences in the coordination geometry are also found in the monomeric niobium(V) and molybdenum(V) porphinato derivatives. Mo(O)(NCS)(TPP) is six-coordinate with the molybdenum atom nearly centered in the porphinato plane.[35] As has already been noted, $Nb(O)(O_2CCH_3)(TPP)$[14] uses the same coordination polyhedron as $O_3Nb_2(TPP)_2$.

There appear to be three effects that, either individually or in some combination, may be important in leading to different structures for the oxo derivatives of niobium(V) and molybdenum(V) porphyrins. These are (1) the size of the metal atoms, (2) the relative importance of π bonding to the oxo ligands, and (3) the importance of metal–ligand π bonding.

As is clear from the structure of $O_3Mo_2(TPP)_2$, a substantial radial expansion of the porphinato ligand is required to accommodate the Mo(V) atom in its nearly centered position with respect to the porphinato ligand. The size of the Nb(V) atom is at least as large as the Mo(V) atom and is probably larger. If the Nb(V) atom is larger, it may simply not fit into the central hole of the porphinato core and be forced to take an out-of-plane position. A small metal displacement and a relatively expanded core are probably energetically less favorable than a large metal displacement and a hole size consistent with minimum strain in the macrocycle. However, even if the Nb(V) atom is no larger than the Mo(V) atom, a substantial radial expansion must occur if the metal is to be centered in the core. Since the expansion of the core must be energetically demanding, it must be compensated for, presumably by the interaction of the metal atom with the porphinato ligand. An alternate structure could occur if the interaction of the Nb(V) atom with the ligand were insufficient.

The stoichiometry of the $O_3M_2(TPP)_2$ complexes requires one oxo ligand to form a bridged linkage. Multiple bonding to the remaining oxo ligands appears to be most developed in the $O_3Mo_2(TPP)_2$ structure with its terminal Mo═O groups and less so in the $O_3Nb_2(TPP)_2$ structure. These relative tendencies to form multiple Mo—O bonds appear generally true for all Mo(V) vs. Nb(V) complexes. Moreover, the C_{4v} symmetry of the coordination group in the oxomolybdenum(V) porphyrins allows the fullest possible amount of π bonding in the entire molecule. The $4d_{xz}$ and $4d_{yz}$ orbitals of molybdenum are fully available for accepting charge from the oxo ligands, principally the terminal oxo ligand; the $4d_{xz}$ and $4d_{yz}$ orbitals may then simultaneously act as charge donors to the π^* orbitals of the porphyrin ligand. While the arrangement of ligands in the niobium complex can still allow for substantial Nb–O π bonding, particularly to the shortest Nb–O bond, it cannot accommodate metal → porphyrin π^* bonding. Presumably the relative porphyrin–metal orbital energies are much more favorable for molybdenum than for niobium. These differences in the relative tendencies of metal → porphyrin π^* bonding could lead to the quite different molybdenum(V) and niobium(V) porphyrin structures.

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Registry No. $O_3Mo_2(TPP)_2$, 61747-27-1; $O_3Nb_2(TPP)_2$, 61703-47-7.

Supplementary Material Available: Tables III and V (anisotropic temperature factors), Tables VII and VIII (bond distances and angles in the porphinato core in $O_3Nb_2(TPP)_2$), and Tables XI and XII (bond distances and angles in the porphinato core of $O_3Mo_2(TPP)_2$) and listings of observed and calculated structure factor amplitudes (×10) for both compounds (72 pages). Ordering information is given on any current masthead page.

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