to a more planar conformation on oxygenation thereby triggering a protein conformational change.[9–18] Although the iron displacement in deoxy hemoglobin is clearly not as extreme as that of Pb in PbTPrP, a *folding* of the porphyrin along the C_α–C_γ axis, because of constraints imposed peripherally by the protein and axially via the proximal histidine, has not been previously considered for deoxy hemoglobin. The results presented here indicate that such bending has no major effect on bond distances and angles[32] and suggest that a "roof" structure may be an alternate possibility. Existing X-ray results on deoxy hemoglobin and myoglobin do not exclude such a conformation.[33,34] Furthermore, analysis[35] of the atomic coordinates[36] obtained from the 1.4-Å resolution study of erythrocruorin, the monomeric hemoglobin found in the insect *Chironomus thummi thummi*, clearly indicates that a dominant distortion of its deoxy form is indeed a folding of the macrocycle along its C_α–C_γ axis with an angle of 7.2°.

Acknowledgment. We are indebted to Drs. C. J. Fritchie and L. K. Hanson for useful discussions. Support under NIH Grant GM-24385 to G.J.B.W. is gratefully acknowledged. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. EY76-C-02-0016.

Registry No. PbTPrP, 73395-80-9.

Supplementary Material Available: A table of fractional coordinates for the hydrogen atoms and a listing of observed and calculated squared structure factors (33 pages). Ordering information is on any current masthead page.

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(32) As noted above, incorporation of the Pb has no major effect on these parameters when compared to H_2TPrP. The core is expanded relative to CuTPrP.

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Molecular and Crystal Structure of a Metalloporphyrin Containing the MoO_2^{2+} Unit: *cis*-Dioxo(5,10,15,20-tetra-*p*-tolylporphyrinato)molybdenum(VI), MoO_2(TTP)

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The molecular structure of MoO_2(TTP), where TTP is the dianion of 5,10,15,20-tetra-*p*-tolylporphyrin, has been determined from X-ray single-crystal analysis. The complex crystallizes in the triclinic $P\bar{1}$ space group with a = 11.554 (3) Å, b = 13.128 (5) Å, c = 16.794 (4) Å, α = 108.04 (2)°, β = 92.09 (2)°, γ = 108.37 (3)°, and Z = 2 formula units per unit cell. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement has led to a final value of R (R_w) index of 0.0690 (0.0677) based on 2112 unique reflections. The molybdenum atom is hexacoordinated in a distorted trigonal prism by the four pyrrole nitrogen atoms and the two oxygen atoms. The Mo–O bond lengths in the cis MoO_2 moiety are 1.709 (9) and 1.744 (9) Å. Two sets of Mo–N distances are observed: Mo–N_1 = 2.245 (9), Mo–N_3 = 2.247 (9) Å; Mo–N_2 = 2.165 (6), Mo–N_4 = 2.149 (7) Å. The molybdenum atom lies 1.095 (9) Å out of the mean plane formed by the 20 carbon atoms of the core (C-20). The porphyrin core shows a strong "horse saddle"-type deformation.

In the past few years, synthesis, structural characterization, and reactivity of molybdenum porphyrins have received considerable attention.[1–7] We recently described the photolysis of a diperoxomolybdenum(VI) porphyrin $Mo(O_2)_2$(TTP), affording a complex of molecular formula MoO_2(TTP) for which we proposed a *cis*-dioxomolybdenum(VI) structure.[2c] To the best of our knowledge, if compounds containing the

Table I. Summary of Crystal Data and Intensity Collection

$MoO_2(TTP)\cdot{}^3/_2C_7H_8$	
mol wt	935.0
space group	$P\bar{1}$
a, Å	11.554 (3)
b, Å	13.128 (5)
c, Å	16.794 (4)
α, deg	108.04 (2)
β, deg	92.09 (2)
γ, deg	108.37 (3)
V, Å^3	2273.0
cell content	2 ($C_{48}H_{36}N_4O_2Mo\cdot{}^3/_2C_7H_8$)
ρ(calcd), g cm^{-3}	1.37
ρ(obsd, flotation), g cm^{-3}	1.4
cryst dimens, mm	0.3 × 0.3 × 0.2
μ, cm^{-1}	3.27
scan speed, deg min^{-1}	10.06–2.51 (most at 2.87)
measd reflctns	6855
obsd reflctns used	2112, $I > 2\sigma(I)$
refined scale factor	0.1548 (62)

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cis-MoO_2^{2+} unit are well-known,[8,9] such complexes with a quadridentate planar ligand have not yet been reported.[10] Only very recently another example of a metalloporphyrin having a *cis*-bis(monodentate) axial ligation has been characterized.[3d]

Herein, we report the determination of the complete molecular structure of MoO_2(TTP) which fully confirms our previous suggestion.[11]

Experimental Section

MoO_2(TTP) was prepared as previously reported.[2c] Crystals suitable for X-ray diffraction studies were obtained by evaporation of a toluene solution under a slow stream of argon. The crystal was carefully mounted on a 0.2-mm glass rod since the crystals are very brittle and invariably fell apart when attempts to fix them in a Lindemann glass capillary were made.

Crystallographic Data. Collection and Reduction of Data. Several single crystals were mounted on a Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP 8/a computer, using Mo Kα radiation from a highly oriented graphite-crystal monochromator. All these samples exhibited triclinic symmetry $P\bar{1}$, and a close interpretation of the Niggli values showed that the unit cell described in Table I could not be reduced to a higher symmetry. The orientation matrix was refined by least-squares computations using 25 reflections. Diffraction data were collected at 291 ± 1 K by using the ω–2θ scan technique for the $1 < \theta < 25°$ range. The scan widths, (SW) were calculated from SW = $(1.4 + 0.5 \tan \theta)°$. The calculated scan angle was extended at each side by 25% for background determination. The net count was then calculated as NC = $I - 2(\mathrm{LB} + \mathrm{RB})$, where I, LB, and RB are respectively the integrated peak intensity, the left background, and the right background. Reflections were considered as insignificant if a rapid prescan was less than 10 counts above the background. In order to detect possible deterioration of the crystal, we periodically checked three reflections every hour. Data reduction yielded 2112 unique reflections in the half reflection sphere (hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$ triplets). The presence of a symmetry center has been confirmed by inspection of the intensities corresponding to 12 hkl, $\bar{h}\bar{k}\bar{l}$ reflection pairs measured in data collection conditions. The observed data were corrected by application of standard Lorentz and polarization factors, and absorption was neglected ($\mu r = 0.042$).

Solution and Refinement of the Structure. The structure was solved by the usual heavy-atom method.[12] After the positional and thermal parameters of the molybdenum atom were refined, a subsequent Fourier transform revealed all the atoms of the porphyrin core and some carbon atoms of the four tolyl groups. The atomic coordinates and the isotropic thermal parameters were refined by minimizing $\sum w(|F_o| - |F_c|)^2$, the weighting function being $w = (2|F_o|_{\min} + |F_o| + 2F_o^2/|F_o|_{\max})^{-1}$. The remaining carbon atoms could then be localized, and it was found that several residual electron density peaks could be interpreted as the presence of two toluene solvation molecules, one of which is in a disordered state around the $(0, {}^1/_2, {}^1/_2)$ symmetry center, conducting thus to the gross formula $C_{48}H_{36}N_4O_2Mo\cdot{}^3/_2C_7H_8$. In the later stages of the structure solution, the anisotropic thermal parameters were introduced for the molybdenum atom together with the weighting function $w = (a + b|F_o|)^2$.[13] All the refinements were performed by using least-squares full-matrix calculations. Finally, the hydrogen atoms corresponding to the porphyrin core and the aromatic tolyl groups were included in the refinements as fixed parameters ($d_{\mathrm{C-H}} = 1.0$ Å; $B = 5.0$ Å^2). The final R value $(\sum(|F_o| - |F_c|))/(\sum|F_o|)$ was 0.0690, and the R_w value $(\sum w(|F_o| - |F_c|)^2)/(\sum F_o^2)^{1/2}$ was 0.0677. A final difference-Fourier map exhibited no peaks larger than 0.7 Å^{-3}, the largest ones corresponding to residual electron densities in the methyl-group regions.

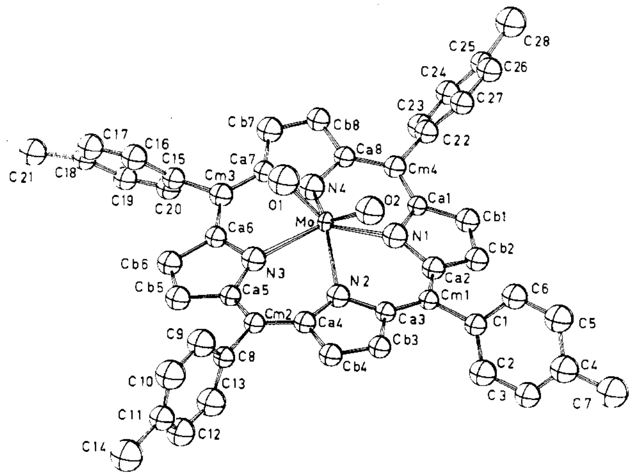

Figure 1. View of the MoO_2(TTP) molecule. Hydrogen atoms have been omitted, and thermal ellipsoids are drawn at the 50% probability level.

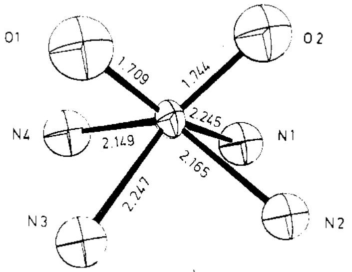

Figure 2. Coordination polyhedron of the molybdenum atom in the MoO_2(TTP) molecule.

The final atomic coordinates and the associated isotropic thermal parameters are listed in Table II. A listing of the observed and calculated structure amplitudes is available as supplementary material.

Description of the Structure and Discussion

The crystal structure consists of discrete MoO_2(TTP) molecules as shown in Figure 1. Relevant interatomic distances and angles are given in Table III. Figure 2 is the coordination polyhedron of the molybdenum atom, which can best be described as a strongly distorted trigonal prism of C_1 symmetry, the four pyrrole nitrogens forming a square face of the prism and the two oxygen being located in a cis position along an edge. The O_1–O_2 distance is 2.547 (13) Å, clearly larger than a peroxide O–O bond length, i.e., 1.40–1.55 Å.[14] A possible structure of peroxomolybdenum(IV) porphyrin for MoO_2(TTP) is thus definitely ruled out. On the other hand, the Mo–O_1 and Mo–O_2 distances, respectively 1.709 (9) and 1.744 (9) Å, are within the range of values associated with a multiple molybdenum–oxygen bond[15] and compare well with those reported for *cis*-dioxomolybdenum(VI) complexes.[8,9] The four Mo–N bond lengths are respectively Mo–N_1 = 2.245

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Table II. Positional and Isotropic Thermal Parameters[a, b]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Mo	0.37281 (9)	0.03509 (8)	0.19406 (7)	0.9[c]	C9	0.6643 (12)	0.1146 (10)	0.5021 (8)	4.9 (6)
O1	0.2615 (8)	−0.0318 (7)	0.2432 (5)	6.0 (4)	C10	0.7409 (12)	0.1323 (11)	0.5751 (8)	5.3 (6)
O2	0.3433 (7)	0.1630 (7)	0.2256 (5)	5.2 (4)	C11	0.8516 (10)	0.1302 (9)	0.5710 (7)	3.8 (5)
N1	0.4168 (7)	0.0900 (6)	0.0814 (5)	4.0 (3)	C12	0.8922 (11)	0.1054 (10)	0.4960 (8)	4.8 (5)
N2	0.5607 (6)	0.1490 (6)	0.2430 (5)	3.3 (3)	C13	0.8212 (12)	0.0870 (10)	0.4218 (8)	5.0 (8)
N3	0.4645 (7)	−0.0747 (6)	0.2309 (5)	3.7 (3)	C14	0.9407 (13)	0.1527 (12)	0.6561 (9)	6.3 (7)
N4	0.2886 (7)	−0.1187 (7)	0.0876 (5)	4.2 (3)	C15	0.2601 (9)	−0.3866 (8)	0.1395 (6)	3.0 (4)
Ca1	0.3444 (8)	0.0494 (8)	0.0039 (5)	2.3 (4)	C16	0.2011 (10)	−0.4281 (9)	0.1991 (7)	4.1 (5)
Cb1	0.3863 (9)	0.1249 (8)	−0.0426 (6)	3.5 (4)	C17	0.1739 (10)	−0.5421 (9)	0.1898 (7)	4.1 (5)
Cb2	0.4832 (9)	0.2179 (8)	0.0112 (6)	3.4 (4)	C18	0.2085 (9)	−0.6147 (8)	0.1243 (6)	3.1 (4)
Ca2	0.5002 (9)	0.2008 (8)	0.0891 (6)	3.2 (4)	C19	0.2630 (9)	−0.5702 (8)	0.0653 (6)	3.4 (4)
Cm1	0.5777 (8)	0.2765 (8)	0.1610 (6)	2.4 (4)	C20	0.2872 (9)	−0.4581 (8)	0.0745 (6)	3.5 (4)
Ca3	0.6040 (8)	0.2548 (8)	0.2324 (6)	2.6 (4)	C21	0.1901 (11)	−0.7395 (10)	0.1197 (7)	4.5 (5)
Cb3	0.6901 (9)	0.3301 (8)	0.3051 (6)	3.1 (4)	C22	0.1606 (9)	−0.0719 (8)	−0.1033 (6)	3.4 (4)
Cb4	0.7067 (9)	0.2730 (6)	0.3568 (6)	3.3 (4)	C23	0.1517 (10)	−0.1591 (9)	−0.1758 (7)	4.1 (5)
Ca4	0.6242 (9)	0.1573 (8)	0.3156 (6)	3.0 (4)	C24	0.0695 (9)	−0.1835 (8)	−0.2469 (7)	3.6 (4)
Cm2	0.6231 (8)	0.0684 (8)	0.3425 (6)	2.7 (4)	C25	−0.0058 (9)	−0.1198 (8)	−0.2467 (6)	3.2 (4)
Ca5	0.5540 (8)	−0.0427 (8)	0.2988 (6)	2.7 (4)	C26	0.0077 (10)	−0.0278 (9)	−0.1736 (7)	3.8 (5)
Cb5	0.5575 (9)	−0.1393 (9)	0.3213 (7)	3.7 (5)	C27	0.0873 (9)	−0.0038 (8)	−0.1026 (6)	3.4 (4)
Cb6	0.4699 (9)	−0.2307 (9)	0.2652 (7)	3.6 (4)	C28	−0.1054 (12)	−0.1509 (11)	−0.3247 (8)	5.6 (6)
Ca6	0.4079 (9)	−0.1919 (8)	0.2105 (6)	2.8 (4)	C29	0.4195 (19)	0.2594 (18)	0.4741 (12)	10.7 (9)
Cm3	0.3027 (9)	−0.2593 (8)	0.1513 (6)	3.4 (4)	C30	0.5018 (17)	0.3541 (17)	0.5193 (12)	9.9 (9)
Ca7	0.2472 (9)	−0.2267 (8)	0.0958 (6)	2.8 (4)	C31	0.4682 (17)	0.4106 (15)	0.5937 (12)	9.4 (9)
Cb7	0.1433 (10)	−0.2927 (9)	0.0371 (7)	4.0 (5)	C32	0.3681 (13)	0.3769 (12)	0.6271 (9)	7.1 (7)
Cb8	0.1204 (9)	−0.2352 (8)	−0.0127 (6)	3.3 (4)	C33	0.2822 (16)	0.2715 (15)	0.5742 (11)	9.0 (8)
Ca8	0.2159 (8)	−0.1286 (8)	0.0164 (6)	2.7 (4)	C34	0.3044 (17)	0.1986 (16)	0.4939 (12)	10.3 (9)
Cm4	0.2457 (9)	−0.0478 (8)	−0.0237 (6)	3.0 (4)	C35	0.5718 (27)	0.5409 (26)	0.6439 (19)	18 (2)
C1	0.6434 (9)	0.3935 (8)	0.1586 (6)	3.0 (4)	C36	−0.0013 (27)	0.4291 (20)	0.5923 (16)	12 (1)
C2	0.7675 (10)	0.4434 (9)	0.1686 (7)	4.4 (5)	C37	−0.1135 (24)	0.5123 (23)	0.5697 (17)	10 (1)
C3	0.8261 (10)	0.5550 (9)	0.1675 (7)	3.9 (5)	C38	−0.0971 (34)	0.5655 (33)	0.5022 (26)	11 (2)
C4	0.7611 (11)	0.6183 (10)	0.1605 (8)	4.7 (5)	C39	0.0011 (20)	0.5327 (19)	0.4631 (15)	6.9 (9)
C5	0.6304 (11)	0.5705 (10)	0.1498 (8)	4.9 (5)	C40	0.0549 (26)	0.4641 (21)	0.4744 (17)	7.8 (9)
C6	0.5722 (10)	0.4573 (9)	0.1480 (7)	3.9 (5)	C41	0.0664 (47)	0.4145 (36)	0.5389 (31)	14 (3)
C7	0.8215 (12)	0.7407 (11)	0.1629 (8)	6.0 (6)	C42	0.0699 (27)	0.5544 (22)	0.4120 (16)	13 (1)
C8	0.7062 (9)	0.0957 (8)	0.4234 (6)	2.8 (4)					
Hb1	0.352	0.117	−0.106	5.0	H16	0.178	−0.374	0.249	
Hb2	0.535	0.289	−0.002		H17	0.128	−0.574	0.234	
Hb3	0.738	0.416	0.317		H19	0.288	−0.620	0.015	
Hb4	0.768	0.309	0.415		H20	0.328	−0.428	0.032	
Hb5	0.619	−0.142	0.370		H23	0.206	−0.208	−0.177	
Hb6	0.450	−0.314	0.264		H24	0.062	−0.249	−0.301	
Hb7	0.090	−0.371	0.028		H26	−0.045	0.021	−0.173	
Hb8	0.049	−0.306	−0.062		H27	0.094	0.061	−0.049	
H2	0.819	0.398	0.174		H29	0.241	0.118	0.456	
H3	0.918	0.590	0.173		H30	0.439	0.221	0.421	
H5	0.580	0.618	0.142		H31	0.582	0.384	0.499	
H6	0.478	0.422	0.140		H33	0.351	0.424	0.685	
H9	0.579	0.118	0.508		H34	0.203	0.243	0.593	
H10	0.713	0.149	0.631		Ct	0.4327 (7)	0.0114 (7)	0.1607 (5)	
H12	0.974	0.101	0.492		C-20	0.4402 (8)	0.0079 (8)	0.1568 (6)	
H13	0.854	0.068	0.365						

[a] Esd's shown in parentheses have been adjusted to the last digit (or digits) of the preceding number (or numbers). [b] Hydrogen atoms were fixed in calculated positions (1-Å unit from their attached carbon with an isotropic thermal parameter of 5.0 Å^2). [c] Anisotropic thermal parameters for the molybdenum atom are B_{11} = 2.42 (4), B_{22} = 1.73 (4), B_{33} = 2.99 (4), B_{12} = 0.66 (2), B_{13} = 0.41 (3), and B_{23} = 1.23 (3) Å^2; these values have been calculated from the refined β_{ij} parameters through $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$.

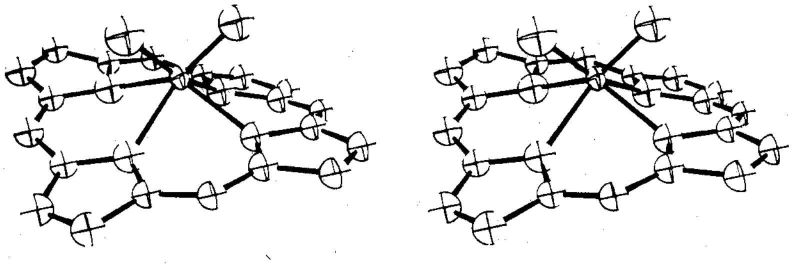

Figure 3. Stereoscopic view of the porphyrin core in the MoO_2(TTP) molecule.

(9), Mo–N_2 = 2.165 (6), Mo–N_3 = 2.247 (9), and Mo–N_4 = 2.149 (7) Å. The molybdenum atom lies 0.972 (9) Å above the mean plane of the four pyrrole nitrogens and 1.095 (9) Å above the C-20 mean plane. A stereoscopic view of the porphyrin core shown on Figure 3 and the formal diagram displaying the perpendicular displacement of each atom from the C-20 mean plane in units of 0.01 Å on Figure 4 clearly exhibit a strong "*horse saddle*"-type deviation from planarity.

Table III. Distances (A) and Angles (Deg)

I. Intramolecular Distances and Angles

Mo Polyhedron

Mo-O1	1.709 (9)	Mo-C-20	1.095 (9)
Mo-O2	1.744 (9)	O1-O2	2.547 (13)
Mo-N1	2.245 (9)	O1-N3	2.580 (13)
Mo-N2	2.165 (6)	O1-N4	2.582 (11)
Mo-N3	2.247 (9)	O2-N1	2.594 (12)
Mo-N4	2.149 (7)	O2-N2	2.588 (12)
Mo-Ct	0.972 (9)		

O1-Mo-O2	95.1 (4)	N4-Mo-N1	76.1 (3)
N1-Mo-N2	81.5 (3)	N3-O1-N4	67.8 (3)
N2-Mo-N3	76.5 (3)	N1-O2-N2	67.5 (3)
N3-Mo-N4	81.8 (3)		

Porphine Core

N1-Ca1	1.374 (11)	N3-Ca5	1.375 (12)
Ca1-Cb1	1.425 (15)	Ca5-Cb5	1.443 (18)
Cb1-Cb2	1.394 (11)	Cb5-Cb6	1.348 (12)
Cb2-Ca2	1.411 (16)	Cb6-Ca6	1.445 (18)
Ca2-N1	1.433 (12)	Ca6-N3	1.391 (12)
Ca2-Cm1	1.366 (11)	Ca6-Cm3	1.392 (12)
Cm1-Ca3	1.361 (16)	Cm3-Ca7	1.356 (17)
N2-Ca3	1.390 (14)	N4-Ca7	1.399 (14)
Ca3-Cb3	1.415 (11)	Ca7-Cb7	1.376 (13)
Cb3-Cb4	1.354 (17)	Cb7-Cb8	1.357 (18)
Cb4-Ca4	1.443 (12)	Cb8-Ca8	1.407 (11)
Ca4-N2	1.356 (14)	Ca8-N4	1.383 (14)
Ca4-Cm2	1.373 (17)	Ca8-Cm4	1.388 (16)
Cm2-Ca5	1.365 (11)	Cm4-Ca1	1.350 (11)

Mo-N1-Ca1	127.4 (6)	Mo-N3-Ca5	127.6 (6)
Mo-N1-Ca2	122.5 (6)	Mo-N3-Ca6	122.9 (6)
Ca1-N1-Ca2	106.1 (8)	Ca5-N3-Ca6	105.1 (8)
N1-Ca1-Cb1	110.8 (8)	N3-Ca5-Cm2	123.0 (9)
Ca1-Cb1-Cb2	105.9 (9)	N3-Ca6-Cm3	125.3 (9)
Cb1-Cb2-Ca2	109.0 (9)	N3-Ca5-Cb5	111.6 (9)
Cb2-Ca2-N1	107.8 (9)	Cm2-Ca5-Cb5	125.2 (9)
N1-Ca2-Cm1	125.0 (9)	N3-Ca6-Cb6	109.1 (9)
Cb2-Ca2-Cm1	127 (1)	Cb6-Ca6-Cm3	125 (1)
Ca2-Cm1-Ca3	127 (1)	Ca5-Cb5-Cb6	106 (1)
Cb1-Ca1-Cm4	124.7 (9)	Cb5-Cb6-Ca6	109 (1)
N1-Ca1-Cm4	124.5 (9)	Ca6-Cm3-Ca7	127 (1)
Ca2-Cm1-C1	115.9 (9)	Ca6-Cm3-C15	115.0 (9)
Ca3-Cm1-C1	117.5 (9)	Ca7-Cm3-C15	117.7 (9)

Mo-N2-Ca3	121.2 (6)	Mo-N4-Ca7	122.6 (7)
Mo-N2-Ca4	123.6 (6)	Mo-N4-Ca8	125.5 (7)
Ca3-N2-Ca4	107.7 (8)	Ca7-N4-Ca8	105.3 (8)
N2-Ca3-Cb3	107.0 (8)	Cm3-Ca7-Cb7	127 (1)
N2-Ca3-Cm1	125.4 (9)	N4-Ca7-Cm3	125.1 (9)
Cm1-Ca3-Cb3	127.2 (9)	N4-Ca7-Cb7	107.9 (9)
Ca3-Cb3-Cb4	110.2 (9)	Cb8-Ca8-Cm4	126.7 (9)
Cb3-Cb4-Ca4	105.0 (9)	N4-Ca8-Cb8	110.3 (9)
Cb4-Ca4-Cm2	123.5 (9)	N4-Ca8-Cm4	122.6 (9)
Cb4-Ca4-N2	109.9 (9)	Ca7-Cb7-Cb8	111 (1)
N2-Ca4-Cm2	126.2 (9)	Cb7-Cb8-Ca8	105.1 (9)
Ca4-Cm2-C8	117.7 (9)	Ca1-Cm4-Ca8	124 (1)
Ca5-Cm2-C8	118.8 (9)	Ca1-Cm4-C22	118.9 (9)
Ca4-Cm2-Ca5	123.5 (9)	Ca8-Cm4-C22	117.0 (9)

Tolyl Groups

Cm1-C1	1.498 (14)	Cm1-C1-C2	125 (1)
C1-C2	1.355 (14)	Cm1-C1-C6	117.7 (9)
C2-C3	1.413 (16)	C2-C1-C6	117 (1)
C3-C4	1.310 (21)	C1-C2-C3	123 (1)
C4-C5	1.421 (17)	C2-C3-C4	121 (1)
C5-C6	1.415 (17)	C3-C4-C5	119 (1)
C6-C1	1.388 (18)	C4-C5-C6	120 (1)
C4-C7	1.524 (19)	C5-C6-C1	120 (1)
		C3-C4-C7	122 (1)
		C5-C4-C7	119 (1)

Tolyl Groups (*Continued*)

Cm2-C8	1.511 (14)	Cm2-C8-C9	122 (1)
C8-C9	1.401 (17)	Cm2-C8-C13	121 (1)
C9-C10	1.398 (20)	C9-C8-C13	116 (1)
C10-C11	1.292 (19)	C8-C9-C10	121 (1)
C11-C12	1.341 (18)	C9-C10-C11	120 (1)
C12-C13	1.378 (19)	C10-C11-C12	120 (1)
C13-C8	1.370 (18)	C11-C12-C13	122 (1)
C11-C14	1.622 (19)	C12-C13-C8	120 (1)
		C10-C11-C14	120 (1)
		C12-C11-C14	119 (1)

Cm3-C15	1.531 (15)	Cm3-C15-C16	121.3 (9)
C15-C16	1.385 (16)	Cm3-C15-C20	120 (1)
C16-C17	1.385 (17)	C16-C15-C20	119 (1)
C17-C18	1.379 (15)	C15-C16-C17	119 (1)
C18-C19	1.375 (15)	C16-C17-C18	122 (1)
C19-C20	1.366 (15)	C17-C18-C19	117 (1)
C20-C15	1.322 (14)	C18-C19-C20	121 (1)
C18-C21	1.561 (18)	C19-C20-C15	123 (1)
		C17-C18-C21	121.0 (9)
		C19-C18-C21	122.2 (9)

Cm4-C22	1.517 (15)	Cm4-C22-C23	122 (1)
C22-C23	1.363 (13)	Cm4-C22-C27	119.6 (9)
C23-C24	1.385 (16)	C23-C22-C27	119 (1)
C24-C25	1.383 (17)	C22-C23-C24	121 (1)
C25-C26	1.393 (13)	C23-C24-C25	121 (1)
C26-C27	1.368 (15)	C24-C25-C26	117 (1)
C27-C22	1.410 (17)	C25-C26-C27	122 (1)
C25-C28	1.572 (17)	C26-C27-C22	120 (1)
		C24-C25-C28	122 (1)
		C26-C25-C28	121 (1)

Toluenes of Crystallization[a]

C29-C30	1.282 (23)	C36-C37	2.033 (48)
C30-C31	1.380 (27)	C37-C38	1.494 (66)
C31-C32	1.314 (25)	C38-C39	1.446 (50)
C32-C33	1.413 (18)	C39-C40	1.298 (44)
C33-C34	1.477 (26)	C40-C41	1.448 (67)
C34-C29	1.430 (28)	C41-C36	1.222 (62)
C31-C35	1.677 (29)	C40-C42	1.785 (45)

C29-C30-C31	115 (2)	C33-C34-C29	108 (2)
C30-C31-C32	129 (2)	C34-C29-C30	129 (2)
C31-C32-C33	113 (2)	C30-C31-C35	113 (2)
C32-C33-C34	125 (2)	C32-C31-C35	118 (2)

Average Distances

N-Ca	1.388 (13)	Cm-Car	1.513 (14)
Ca-Cb	1.421 (14)	Car-Car	1.375 (16)[b]
Cb-Cb	1.363 (14)	Car-CH_3	1.570 (18)[b]
Ca-Cm	1.369 (14)		

II. Intermolecular Distances[c]

atoms	trans	dist	atoms	trans	dist
O1· · ·C14	2 1 0 1	3.23 (2)	Cb2· · ·Ca7	2 1 0 0	3.64 (1)
O2· · ·C21	1 0 1 0	3.25 (2)	Ca3· · ·C23	2 1 0 0	3.48 (2)
O2· · ·C35	2 1 1 1	3.61 (3)	Cb3· · ·C23	2 1 0 0	3.60 (2)
N2· · ·C23	2 1 0 0	3.52 (1)	Cb4· · ·C23	2 1 0 0	3.64 (1)
N3· · ·Cb1	2 1 0 0	3.64 (1)	Cb4· · ·C24	2 1 0 0	3.52 (2)
N4· · ·Cb2	2 1 0 0	3.54 (1)	Ca4· · ·C23	2 1 0 0	3.56 (2)

[a] The angles corresponding to the second toluene of crystallization are not given. [b] Distances between the aryl carbons of the second toluene of crystallization are not included. The same remark holds for the Car-CH_3 distance of the second toluene. [c] The transformation of the second atom is given by a four-digit code. The first represents the equipoint (see below) while the second through fourth represent the addition (+1) of unit cell vectors *a*, *b*, and *c*. Transformation code: (1) *x*, *y*, *z*; (2) −*x*, −*y*, −*z*.

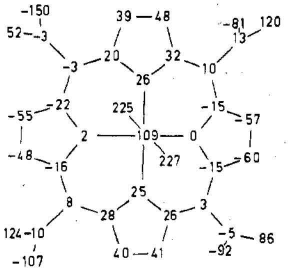

Figure 4. Formal diagram of the porphyrin core displaying the perpendicular displacement of each atom from the mean (C-20) plane, in units of 0.01 Å.

The pyrrole rings are alternatively tilted up and down with respect to the C-20 mean plane, in a quasi S_4 ruffling.[16,17] Hence, two sets of molybdenum–nitrogen bond distances are observed, a feature which is similary found in $Mo(NO)_2$(TTP).[3d]

The core of the porphyrin exhibits a substantial contraction as shown by the short averaged distance between the center and the pyrrole nitrogens Ct···N = 1.976 (9) Å. This radius is significantly smaller than the value of ≃2.01 Å for which Hoard[16] had estimated that the internal strain into a metalloporphyrin core is minimized. Otherwise, interatomic bond distances and angles compare well with those of other similar metalloporphyrins.

Within experimental errors, the O_1MoO_2 plane is normal to the C-20 mean plane, and the oxygen atoms nearly point toward the meso carbon atoms Cm1 and Cm3. This staggered conformation of the *cis*-dioxo MoO_2 moiety is different from that reported for peroxomolybdenum[3a] and titanium[18] porphyrin complexes, for which the most stable arrangements are obtained when the dioxygen ligand eclipses two opposite nitrogens of the macrocycle.[19] It seems reasonable to assume that oxygen–nitrogen repulsive interactions[20] are minimized by adopting a conformation where the oxygen atoms are located at approximately equal distances, ca. 2.58 Å, from their two neighboring nitrogen atoms. The two eclipsed situations would lead to extremely short intramolecular O···N contacts, respectively 2.13 and 2.37 Å, values which are significantly smaller than the sum of the van der Waals radii of nitrogen and oxygen, i.e., 2.90 Å.[21] In $Mo(O_2)_2$(TTP) a very short O···N distance 2.393 (12) Å between the peroxide oxygen atom and the pyrrole nitrogen atom is associated with a contracted O–O bond length, 1.399 (6) Å.[3e] Possibly for the same reason, in MoO_2(TTP), the O_1–Mo–O_2 angle is constricted to 95.1 (4)°, whereas the usual range of values found in other *cis*-dioxomolybdenum(VI) complexes is 102–114°.[8,9]

Figure 5 illustrates the packing of symmetry-related porphyrin cores in the unit cell. Core 1 is respectively related to core 2 and core 3 through the ($^1/_2$, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) inversion centers. Two main features emerge from this crystal structure. Cores 1 and 2 represent the closest packing of two discrete molecules, and the shortest intermolecular distances between them, given in Table III, range from 3.48 (2) to 3.70 (2) Å. On the other hand, cores 1 and 3 have their oxygen

Table IV

Equations of Least-Squares Planes[a]

atom	D, Å[b]	atom	D, Å
Plane 1: N1-N2-N3-N4 $0.8318X - 0.1141Y - 0.5432Z - 2.7467 = 0$			
N1	0.134 (8)	N3	0.133 (8)
N2	−0.133 (8)	N4	−0.134 (8)
Mo[c]	−0.972 (9)		
Plane 2: N1-Ca1-Cb1-Cb2-Ca2 $0.8653X - 0.3384Y - 0.3699Z - 3.0685 = 0$			
N1	0.035 (8)	Cb2	0.01 (1)
Ca1	−0.03 (1)	Ca2	−0.03 (1)
Cb1	0.01 (1)		
Plane 3: N2-Ca3-Cb3-Cb4-Ca4 $0.8708X - 0.0702Y - 0.4866Z - 3.0962 = 0$			
N2	−0.022 (8)	Cb4	0.002 (11)
Ca3	0.02 (1)	Ca4	0.01 (1)
Cb3	−0.02 (1)		
Plane 4: N3-Ca5-Cb5-Cb6-Ca6 $0.7704X + 0.0846Y - 0.6319Z - 1.7581 = 0$			
N3	0.013 (8)	Cb6	0.02 (1)
Ca5	−0.002 (10)	Ca6	−0.02 (1)
Cb5	−0.01 (1)		
Plane 5: N4-Ca7-Cb7-Cb8-Ca8 $0.7702X - 0.1335Y - 0.6237Z - 2.3505 = 0$			
N4	−0.043 (8)	Cb8	−0.02 (1)
Ca7	0.03 (1)	Ca8	0.04 (1)
Cb7	−0.01 (1)		
Plane 6: C1-C7 $0.1296X - 0.0035Y - 0.9916Z + 1.7440 = 0$			
C1	−0.01 (1)	C5	0.003 (12)
C2	−0.01 (1)	C6	0.01 (1)
C3	0.03 (1)	C7	−0.02 (1)
C4	0.003 (12)		
Plane 7: C8-C14 $-0.0316X - 0.9899Y - 0.1382Z - 0.0855 = 0$			
C8	−0.04 (1)	C12	0.02 (1)
C9	0.01 (1)	C13	0.01 (1)
C10	0.02 (1)	C14	−0.02 (2)
C11	−0.008 (12)		
Plane 8: C15-C21 $-0.8415X - 0.0890Y - 0.5329Z + 4.4314 = 0$			
C15	−0.05 (1)	C19	0.04 (1)
C16	−0.01 (1)	C20	0.001 (11)
C17	0.05 (1)	C21	−0.06 (1)
C18	0.03 (1)		
Plane 9: C22-C28 $0.5421X + 0.7669Y - 0.3434Z - 1.5630 = 0$			
C22	−0.04 (1)	C26	0.04 (1)
C23	0.002 (12)	C27	−0.007 (11)
C24	0.03 (1)	C28	−0.04 (1)
C25	0.02 (1)		
Plane 10: Carbons of the Core, Ca1-Cm4 (C-20 plane)[d] $0.8347X - 0.1172Y - 0.5381Z - 2.8993 = 0$			

Dihedral Angles, Deg

planes	angle	planes	angle
1-2	16.6	1-3	4.7
1-4	13.1	1-5	6.0
1-6	50.2	1-7	81.6
1-8	114.9	1-9	57.3
1-10	0.39		

[a] Planes are defined as $AX + BY + CZ + D = 0$, X, Y, and Z being orthogonalized coordinates. [b] Distance of a given atom from the mean plane. [c] Atoms not included in the calculation of the plane. [d] Distances to the C-20 plane are shown in Figure 4.

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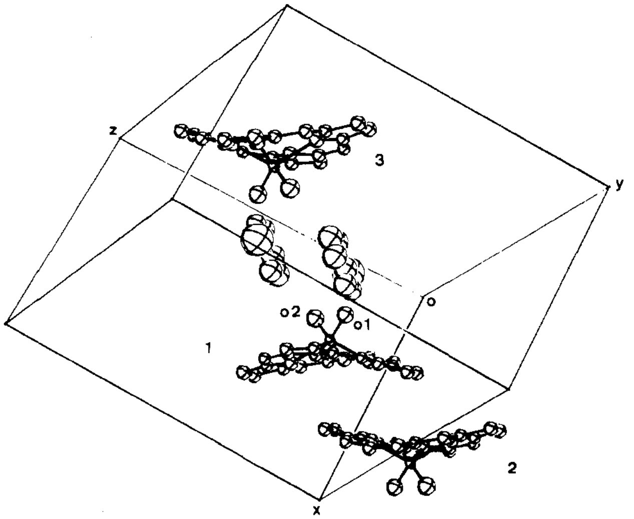

Figure 5. Packing of symmetry-related porphyrin cores in the unit cell.

atoms pointing toward each other and are separated by two symmetry-related toluene molecules of crystallization. Weak interactions occur between the methyl group of the toluene molecule and one of the oxygen atoms of the molybdenyl moiety, evidenced by the $O_2 \cdots C_{35}$ distance 3.61 (3) Å. Even shorter contacts are found between the oxygen atoms and the tolyl methyl groups of neighboring porphyrins: $O_1 \cdots C_{14}$ and $O_2 \cdots C_{21}$ respectively 3.23 (2) and 3.25 (2) Å, ensuring thus the crystal cohesion through weak hydrogen bonds.

The molecular structure of MoO_2(TTP) illustrates well the definite preference of complexes containing the d^0 MoO_2^{2+} unit to adopt a cis geometry,[22] even at the expense of severe deformations of the porphyrin ligand. This is in agreement with the general tendency observed for strong σ- or π-bonding ligands to avoid sharing the same central-atom orbital.[23] The strained situation of the macrocycle is probably kept in solution. An approximate treatment[24] of the temperature-dependent ^{1}H NMR data[3c] gives an activation energy for the rotation of the tolyl groups $\Delta G_c^{\ddagger} = 13.8 \pm 1$ kcal mol^{-1} at the coalescence temperature $T_c = 290$ K. A low value of $\Delta G_c^{\ddagger}$ has been associated in several metalloporphyrins with a significant deviation from planarity of the macrocycle.[25]

The high reactivity of MoO_2(TTP), observed toward oxidation of phosphines,[26] may then be explained by the release of internal strain going from $Mo^{VI}O_2$(TTP) (Mo–Ct = 0.972 Å; Ct···N = 1.967 Å) to $Mo^{IV}O$(TTP) (Mo–Ct = 0.639 Å; Ct···N = 2.011 Å)[3c] during the oxygen atom transfer. Such an enhancement of the oxidizing properties, induced by internal steric-strain factors, may be relevant to the oxidation mechanisms of several metalloenzymes in which *cis*-dioxomolybdenum(VI) complexes are involved.[27] We are currently testing this hypothesis.

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Registry No. $MoO_2(TTP)\cdot{}^3/_2C_7H_8$, 73610-83-0.

Supplementary Material Available: A listing of the observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of $[N(CH_3)_4]_2[Mo_2O_2S_2(S_2)_2]$: A Compound with Two S_2^{2-} Ligands

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The X-ray crystal and molecular structure of $[N(CH_3)_4]_2[Mo_2O_2S_2(S_2)_2]$ has been determined by two independent data collection procedures (I, II). The compound crystallizes in the orthorhombic space group $Pca2_1$ with $Z = 4$. The unit cell dimensions are, for I, $a = 29.202$ (5) Å, $b = 6.546$ (1) Å, and $c = 10.875$ (2) Å and, for II, $a = 29.122$ (5) Å, $b = 6.529$ (1) Å, and $c = 10.884$ (2) Å. Full-matrix least-squares refinement resulted in a final R_1 index of 0.044 (I) or 0.069 (II) for 1774 (I) or 2728 (II) independent data. The structure contains discrete dimeric $[Mo_2O_2S_2(S_2)_2]^{2-}$ anions and $[N(CH_3)_4]^+$ cations. The two S_2^{2-} ligands (S–S = 2.074–2.090 Å) are asymmetrically bonded to the central unit $Mo_2O_2S_2^{2+}$ (Mo–S 2.38 and 2.44 Å), the structure of which (*cis*-dioxo and nonplanar MoS_2Mo bridge) is nearly identical with that of other $Mo_2O_2S_2^{2+}$ compounds. The results indicate that the geometrical data derived from both measurements are internally consistent, although the temperature factors show significant differences.

Introduction

Not many coordination compounds with the disulfur moiety as ligand are known. But the S_2^{2-} complex chemistry is interesting because there is no other simple ligand with such a large variety of modes of coordination.[2] The basic structural types are the side-on coordination (MS_2) and the bridging type (MS_2M). An interesting type of coordination occurs in $[Mo_4(NO)_4S_{13}]^{4-}$ where four S_2^{2-} ligands are side-on and

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