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Molybdenum(IV)–Porphyrin Derivatives: Oxo(5,10,15,20-tetra-p-tolylporphyrinato)molybdenum(IV), MoO(TTP), and Dichloro(5,10,15,20-tetra-p-tolylporphyrinato)molybdenum(IV), Mo(Cl)2(TTP). Syntheses and Structures

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Reaction of gaseous hydrogen chloride with the oxomolybdenum(IV) porphyrin complex MoO(TTP) under mild conditions affords the corresponding dichloromolybdenum(IV) complex Mo(Cl)2(TTP), where TTP is the dianion of 5,10,15,20-tetra-p-tolylporphyrin. The molecular stereochemistry of both compounds has been determined by X-ray diffraction techniques using counter data. Crystal data are as follows. Compound I: MoO(TTP), monoclinic, space group $P2_1/c$, $Z = 4$, $a = 17.420$ (6) Å, $b = 16.851$ (6) Å, $c = 15.734$ (5) Å, $\beta = 112.23$ (4)°. Compound II: Mo(Cl)2(TTP), orthorhombic, space group $Fdd2$, $Z = 16$, $a = 45.159$ (9) Å, $b = 35.671$ (7) Å, $c = 11.199$ (3) Å. Refinement of compound I was based on 2859 observed data; the final discrepancy indices were $R_1 = 0.069$ and $R_2 = 0.084$. The molybdenum atom is pentacoordinated by the four pyrrole nitrogen atoms and the apical oxygen atom. The Mo–O bond length is 1.656 (6) Å and the average Mo–N bond distance is 2.110 (6) Å. The molybdenum atom lies 0.6389 (8) Å out of the mean plane of the four nitrogen atoms toward the oxygen atom. The porphyrin shows a slight doming characteristic of five-coordinate metalloporphyrins. Refinement of compound II was based on 1977 observed data; the final discrepancy indices were $R_1 = 0.053$ and $R_2 = 0.063$. The molybdenum atom is hexacoordinated by the four pyrrole nitrogen atoms and two chlorine atoms. The average Mo–N bond length is 2.074 (6) Å. The two chlorine atoms are mutually trans with regard to the porphyrin, and the Cl(1)–Mo–Cl(2) bond angle is equal to 178.4 (2)°. Although chemically equivalent, the two Mo–Cl distances appear to be somewhat different: Mo–Cl(1) = 2.347 (4) Å, Mo–Cl(2) = 2.276 (4) Å. The porphyrin skeleton is planar within experimental error and contains the molybdenum atom. Internal parameters of the porphyrin correspond to an expanded core like that found in Sn(Cl)2(TTP).

Except for the diperoxo derivative Mo(O2)2(TTP),[1] all of the known molybdenum–porphyrin derivatives are oxo compounds whose chemistry is dominated by the presence of very strong Mo=O bonding.[2] We now report the synthesis of a non-oxo molybdenum derivative, namely, the dichloro compound Mo(Cl)2(TTP) obtained from the oxo compound MoO(TTP) as starting material. Structural characterization of both compounds is reported here. As expected, the dichloro compound is a useful precursor to low-valent molybdenum–porphyrin derivatives.[3]

Experimental Section

General Procedures. All reagents were at least of reagent grade quality. All solvents were distilled and stored under argon. Mesotetra-p-tolylporphine (TTPH2) was prepared and purified by the method of Adler et al.[4] Amalgamated zinc was freshly prepared before use by washing granulated zinc with a dilute solution of hydrochloric acid, treating the zinc with a dilute solution of mercury(II) chloride, and subsequently washing with distilled water. Gaseous hydrogen chloride, obtained from Matheson, was used without further purification.

All reactions were carried out under argon by using modified Schlenk tubes. All transfers and manipulations of solid samples were undertaken in a Vacuum Atmospheres inert-atmosphere box with a gas-purifying system (<1 ppm oxygen).

Analyses were performed by the Service Central de Microanalyses du C.N.R.S., Division de Strasbourg, for C, H, and N and by the Division de Thiais for Mo and Cl.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer with Nujol mulls; a polystyrene film was used for calibration. A Polytec Fir 30 interferometer was used in the 400–50-cm⁻¹ region. Proton magnetic resonance spectra (NMR) were obtained at 90 MHz on a Bruker Model WH 90; all spectra were run in saturated deuteriochloroform solutions, and signal multiplicities are reported as s (singlet), d (doublet), t (triplet), and m (multiplet); the chemical shifts are expressed in δ values (ppm) relative to tetramethylsilane as internal standard. Visible spectra were recorded on a Beckman Acta CIII spectrophotometer. Mass spectra were determined on a Thomson-Houston THN 208 spectrometer operating at 70 eV. Paramagnetic susceptibilities were measured at room temperature by the NMR described by Evans.[5] X-ray data were

collected with a Philips PW 1100 automated diffractometer. Computer calculations were performed on the Univac 1108 located at the Centre de Recherches Nucléaires de Cronenbourg, Strasbourg, France.

Oxo(5,10,15,20-tetra-p-tolylporphyrinato)molybdenum(IV)–benzene, MoO(TTP)·C6H6 (I). The starting material used, MoO(Cl)(TTP)·HCl, was prepared by a modified version of the previously described procedure.[2a] An essential modification is the use of MoOCl3 (2–3 mol) rather than the large excess of Mo(CO)6 (10–15 mol) for 1 mol of porphyrin. Mesitylene was also preferred to decalin. Then the resulting yield is excellent (76%). Anal. Calcd for C48H37OCl2N4Mo: C, 67.61; H, 4.37; N, 6.57; Cl, 8.32. Found: C, 65.23; H, 4.76; N, 6.45; Cl, 7.98.

MoO(Cl)(TTP)·HCl (500 mg, 0.58 mmol) and amalgamated zinc (200 mg) were refluxed in dichloromethane (50 mL) for 30 min under argon. The resulting red solution was filtered and then purified by passing it through a column packed with neutral Al2O3 and eluted with benzene. The concentrated solution was mixed with pentane and kept for several days for crystallization. The crystals obtained were filtered, washed with pentane, and dried in vacuo (448 mg, 90% based on transformed starting material). Anal. Calcd for C54H42ON4Mo: C, 75.51; H, 4.93; N, 6.52. Found: C, 74.25; H, 5.48; N, 6.23. IR: $\bar{\nu}_{max}$ 970 cm⁻¹ (Mo=O). NMR: δ 2.72 (s, 12 H, methyl), 7.36 (s, 6 H, benzene), 7.59 (m, 8 H meta, tolyl), 8.05 (d, 4 H ortho, $J = 8$ Hz, tolyl), 8.21 (d, 4 H ortho, $J = 8$ Hz, tolyl), 9.16 (s, 8 H, pyrrole). Visible (CH2Cl2): ν_{max} 431 (10⁻³ϵ 1100), 514 (20), 554 (103), 592 (13) nm. Mass spectrum: m/e 782 (⁹⁸MoO(TTP)⁺, 100%), 766 (⁹⁸Mo(TTP)⁺, 2%). The complex is diamagnetic: $\mu_{eff} = 0.0$ μ_B.

Dichloro(5,10,15,20-tetra-p-tolylporphyrinato)molybdenum(IV)–Benzene, Mo(Cl)2(TTP)·C6H6 (II).[6] Under scrupulously oxygen-free conditions MoO(TTP)·C6H6 (500 mg, 0.58 mmol) was dissolved in benzene (150 mL). Gaseous hydrogen chloride was then bubbled into the stirred solution at ambient temperature for 20 min. The initial red solution rapidly turned to a brown solution. It was concentrated under reduced pressure to ca. 50 mL and kept for crystallization after adding an excess of pentane saturated with gaseous HCl. The crystals produced were collected by filtration, washed with pentane, and dried in vacuo (480 mg, 90%). Anal. Calcd for C54H42Cl2N4Mo: C, 70.98; H, 4.63; N, 6.13; Cl, 7.76; Mo, 10.49. Found: C, 71.65; H, 5.03; N, 6.08; Cl, 6.68; Mo, 10.48. IR: $\bar{\nu}_{max}$ 330 cm⁻¹ (Mo–Cl). NMR: δ 2.46 (s, 12 H, methyl), 7.36 (s, 6 H, benzene), 7.76 (d, 8 H meta, tolyl), 10.06 (d, 8 H ortho, tolyl), 17.54 (s, 8 H, pyrrole). The complex

Table I. Summary of Crystal Data and Intensity Collection

	MoO(TTP)·C_6H_6 (1)	Mo(Cl)$_2$(TTP)· C_6H_6 (II)
formula	$C_{54}H_{42}ON_4Mo$	$C_{54}H_{42}Cl_2N_4Mo$
mol wt	858.9	913.8
space group	$P2_1/c$	$Fdd2$
cell constants		
a, Å	17.420 (6)	45.159 (9)
b, Å	16.851 (6)	35.671 (7)
c, Å	15.734 (5)	11.199 (3)
α, deg	90	90
β, deg	112.23 (4)	90
γ, deg	90	90
V, Å^3	4275.3	18040.1
Z	4	16
ρ(calcd), g cm^{-3}	1.334	1.345
ρ(obsd), g cm^{-3}		1.33 (2), by flotation in $ZnCl_2$ (aq)
crystal dimensions, mm	0.07 × 0.10 × 0.32	0.10 × 0.15 × 0.23
μ, cm^{-1}	29.75	38.99
data collection method	θ–2θ scan	θ–2θ scan
scan mode	step–scan (28 steps)	scanning
scan speed, deg min^{-1}	2.4	1.9
scan range, deg	1.00 + 0.28 tan θ	0.80 + 0.28 tan θ
bkgd counts at both ends of the scan	0	(scan time)/2
θ limits, deg	3–55	2–63
measd reflections	5618	4128
obsd reflections used, $I > 3\sigma(I)$	2859	1977
p value	0.08	0.08
final R_1 $(=\Sigma ||F_o| - |F_c||/\Sigma F_o)$	0.069	0.053
final R_2 $(=[\Sigma w(|F_o| - |F_c|)^2/ \Sigma w|F_o|^2]^{1/2})$	0.084	0.063

is paramagnetic: $\mu_{eff}^{cor} = 2.90$ μ_B. Visible (CH_2Cl_2): ν_{max} 360 (ϵ × 10^{-3} 42) 429 (105), 488 (28), 550 (10) nm.

Crystallographic Data. Crystals were obtained at 5 °C by slow diffusion of pentane in a benzene solution of the complexes. Well-formed crystals suitable for X-ray study were then grown after several weeks under argon. Crystals were sealed in Lindemann glass capillaries and optically aligned on a Philips PW 1100 diffractometer. Preliminary study established monoclinic space group $P2_1/c$ for I and orthorhombic space group $Fdd2$ for II. Unit cell parameters were determined from a least-squares analysis of the θ, χ, and ϕ angles of 25 reflections centered automatically, by using graphite-monochromated Cu Kα radiation. Crystal data are given in Table I.

The diffraction data were collected at room temperature (20 ± 1 °C). During the intensity measurements, three reflections were used for periodic checking (every 90 min) on the alignment and possible deterioration of the crystals; the deviations of these standard reflections were all within counting statistics. The intensity data were reduced to relative squared amplitudes $(F_o)^2$ by application of standard Lorentz and polarization factors. Absorption effects were neglected for both data sets.

Solution and Refinement of the Structures. Both structures were solved by the heavy-atom method. The Mo atoms were located from a three-dimensional Patterson synthesis. Subsequent Fourier and difference Fourier syntheses led to the location of all nonhydrogen atoms. The structures were then refined by full-matrix least-squares techniques. The quantity minimized was $w(|F_o| - |F_c|)^2$, where the weights w were taken as $1/\sigma^2(F_o)$. The usual procedures, computer programs,[7] atomic scattering factors,[8] and anomalous terms[9] were employed. All nonhydrogen atoms were refined by assuming anisotropic thermal motion. The atomic parameters were grouped in several blocks due to limitations of computer memory. Except for the methyl carbons, the hydrogen atoms were included as a fixed contribution before the last cycles, their positions being idealized by assuming a trigonal-planar geometry and by using C–H distance of 1.00 Å. Each hydrogen atom was assigned a thermal parameter of 1.0 Å^2 greater than the isotropic thermal parameter of the carbon to which it is attached. The final agreement values are $R_1 = 0.069$ (I) and 0.053 (II) and $R_2 = 0.084$ (I) and 0.063 (II). The estimated
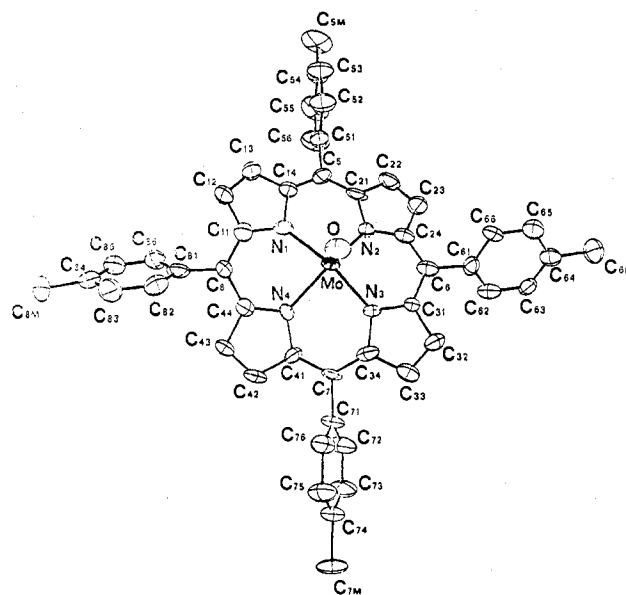

Figure 1. Perspective drawing of the MoO(TTP) molecule as it exists in the crystal. The 50% probability vibrational ellipsoids are shown.
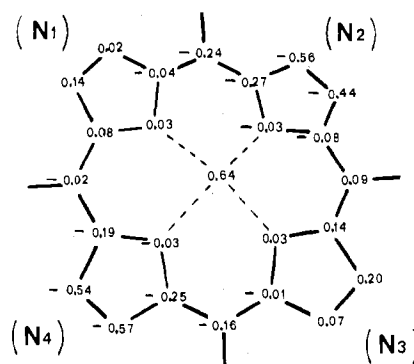

Figure 2. Formal diagram of the porphinato core having the same orientation as Figure 1. Each atom symbol has been replaced by its perpendicular displacement, in units of Å, from the (4N) plane.

standard deviation of an observation of unit weight was 1.47 (I) and 1.12 (II). A listing of the observed and calculated structure amplitudes and a table of positional and thermal parameters are available.[10]

Description of the Structures and Discussion

The Oxo Compound (I). The crystal structure consists of one discrete molecule of MoO(TTP) and one benzene solvate molecule per asymmetric unit cell. A view of the MoO(TTP) molecule with the numbering scheme used is shown in Figure 1. Bond distances and angles are presented in Table II.

The molybdenum atom is pentacoordinated by the four pyrrole nitrogen atoms and the apical oxygen atom. The coordination polyhedron is a pyramid with a square base whose symmetry is close to C_{4v}. The four molybdenum–nitrogen bond lengths are equivalent and the average Mo–N distance is 2.110 (6) Å. The molybdenum–oxygen bond length is 1.656 (6) Å and compares well with the Mo–O distances found in pentacoordinated oxomolybdenum compounds (Table III).

The four pyrrole nitrogens are approximately coplanar. Mean planes were determined by the method of least squares[11] (Table IV). The Mo–O vector is nearly perpendicular to the (4N) plane as shown by the O–Mo–N bond angles and the O⋯N contacts. Figure 2 is a formal diagram of the porphinato core and shows atom displacements from the (4N) plane. The figure is drawn with the same general orientation as Figure 1. Each labeled atom of Figure 1 has been replaced by the

Table II. Molecular Bond Lengths and Angles in MoO(TTP)·C₆H₆ᵃ

Bond Lengths (Å)

Bond	Length	Bond	Length	Bond	Length	Bond	Length
Mo-O	1.656 (6)	N(4)-C(41)	1.404 (13)	C(6)-C(24)	1.402 (14)	C(8)-C(11)	1.403 (17)
Mo-N(1)	2.113 (9)	C(41)-C(42)	1.411 (23)	C(6)-C(31)	1.417 (17)	C(8)-C(44)	1.406 (14)
Mo-N(2)	2.110 (11)	C(42)-C(43)	1.341 (20)	C(6)-C(61)	1.511 (18)	C(8)-C(81)	1.492 (19)
Mo-N(3)	2.104 (9)	C(43)-C(44)	1.446 (19)	C(61)-C(62)	1.389 (14)	C(81)-C(82)	1.379 (16)
Mo-N(4)	2.115 (10)	C(44)-N(4)	1.381 (19)	C(62)-C(63)	1.386 (18)	C(82)-C(83)	1.401 (21)
N(1)-C(11)	1.375 (21)			C(63)-C(64)	1.352 (16)	C(83)-C(84)	1.399 (17)
C(11)-C(12)	1.417 (17)	C(5)-C(14)	1.388 (21)	C(64)-C(65)	1.414 (15)	C(84)-C(85)	1.366 (17)
C(12)-C(13)	1.340 (23)	C(5)-C(21)	1.376 (18)	C(65)-C(66)	1.393 (19)	C(85)-C(86)	1.359 (19)
C(13)-C(14)	1.394 (22)	C(5)-C(51)	1.508 (14)	C(66)-C(61)	1.386 (14)	C(86)-C(81)	1.390 (15)
C(14)-N(1)	1.409 (16)	C(51)-C(52)	1.396 (19)	C(64)-C(6M)	1.566 (20)	C(84)-C(8M)	1.518 (21)
N(2)-C(21)	1.423 (13)	C(52)-C(53)	1.410 (17)				
C(21)-C(22)	1.453 (23)	C(53)-C(54)	1.367 (24)	C(7)-C(34)	1.378 (19)	CB(1)-CB(2)	1.273 (49)
C(22)-C(23)	1.333 (20)	C(54)-C(55)	1.350 (23)	C(7)-C(41)	1.393 (17)	CB(2)-CB(3)	1.372 (40)
C(23)-C(24)	1.445 (18)	C(55)-C(56)	1.438 (19)	C(7)-C(71)	1.500 (13)	CB(3)-CB(4)	1.356 (48)
C(24)-N(2)	1.365 (19)	C(56)-C(51)	1.371 (20)	C(71)-C(72)	1.393 (17)	CB(4)-CB(5)	1.376 (46)
N(3)-C(31)	1.370 (20)	C(54)-C(5M)	1.522 (18)	C(72)-C(73)	1.403 (17)	CB(5)-CB(6)	1.376 (32)
C(31)-C(32)	1.439 (16)			C(73)-C(74)	1.373 (21)	CB(6)-CB(1)	1.339 (40)
C(32)-C(33)	1.359 (23)			C(74)-C(75)	1.357 (20)		
C(33)-C(34)	1.445 (21)			C(75)-C(76)	1.415 (15)		
C(34)-N(3)	1.412 (14)			C(76)-C(71)	1.388 (17)		
				C(74)-C(7M)	1.547 (16)		

Bond Angles (deg)

Angle	deg	Angle	deg	Angle	deg
O-Mo-N(1)	105.54 (41)	Mo-N(3)-C(31)	124.82 (65)	C(24)-C(6)-C(31)	122.96 (1.13)
O-Mo-N(2)	109.57 (41)	Mo-N(3)-C(34)	125.13 (63)	C(24)-C(6)-C(61)	117.73 (1.01)
O-Mo-N(3)	107.73 (42)	N(3)-C(31)-C(32)	111.28 (1.13)	C(31)-C(6)-C(61)	119.28 (1.03)
O-Mo-N(4)	107.55 (40)	C(31)-C(32)-C(33)	106.41 (1.25)	C(6)-C(61)-C(62)	122.66 (98)
N(1)-Mo-N(2)	85.63 (38)	C(32)-C(33)-C(34)	108.06 (1.24)	C(6)-C(61)-C(66)	117.96 (95)
N(2)-Mo-N(3)	83.68 (38)	C(33)-C(34)-N(3)	108.67 (1.10)	C(61)-C(62)-C(63)	120.27 (1.03)
N(3)-Mo-N(4)	83.35 (38)	C(34)-N(3)-C(31)	105.48 (1.08)	C(62)-C(63)-C(64)	121.52 (1.06)
N(4)-Mo-N(1)	84.43 (37)	N(3)-C(31)-C(6)	124.78 (1.07)	C(63)-C(64)-C(65)	118.88 (1.06)
N(1)-Mo-N(3)	146.73 (47)	C(6)-C(31)-C(32)	123.77 (1.17)	C(64)-C(65)-C(66)	120.15 (1.03)
N(2)-Mo-N(4)	142.88 (45)	N(3)-C(34)-C(7)	125.47 (1.04)	C(65)-C(66)-C(61)	119.85 (1.03)
		C(7)-C(34)-C(33)	125.82 (1.16)	C(66)-C(61)-C(62)	119.31 (1.01)
Mo-N(1)-C(11)	125.11 (67)			C(6M)-C(64)-C(63)	121.55 (1.07)
Mo-N(1)-C(14)	126.06 (68)	Mo-N(4)-C(41)	127.15 (63)	C(6M)-C(64)-C(65)	119.50 (1.05)
N(1)-C(11)-C(12)	109.61 (1.18)	Mo-N(4)-C(44)	126.86 (63)		
C(11)-C(12)-C(13)	106.92 (1.32)	N(4)-C(41)-C(42)	108.58 (1.11)	C(34)-C(7)-C(41)	125.16 (1.14)
C(12)-C(13)-C(14)	109.41 (1.36)	C(41)-C(42)-C(43)	109.86 (1.26)	C(34)-C(7)-C(71)	117.88 (1.05)
C(13)-C(14)-N(1)	108.26 (1.19)	C(42)-C(43)-C(44)	105.94 (1.22)	C(41)-C(7)-C(71)	116.92 (1.06)
C(14)-N(1)-C(11)	105.60 (1.17)	C(43)-C(44)-N(4)	109.99 (1.08)	C(7)-C(71)-C(72)	122.09 (1.09)
N(1)-C(11)-C(8)	125.15 (1.10)	C(44)-N(4)-C(41)	105.61 (1.07)	C(7)-C(71)-C(76)	119.12 (1.05)
C(8)-C(11)-C(12)	125.04 (1.22)	N(4)-C(41)-C(7)	125.08 (1.04)	C(71)-C(72)-C(73)	119.01 (1.27)
N(1)-C(14)-C(5)	123.97 (1.11)	C(7)-C(41)-C(42)	126.33 (1.18)	C(72)-C(73)-C(74)	122.33 (1.35)
C(5)-C(14)-C(13)	127.62 (1.27)	N(4)-C(44)-C(8)	125.81 (1.05)	C(73)-C(74)-C(75)	118.60 (1.35)
		C(8)-C(44)-C(43)	124.18 (1.14)	C(74)-C(75)-C(76)	120.93 (1.28)
Mo-N(2)-C(21)	126.31 (62)			C(75)-C(76)-C(71)	120.32 (1.21)
Mo-N(2)-C(24)	126.71 (63)	C(14)-C(5)-C(21)	126.13 (1.21)	C(76)-C(71)-C(72)	118.78 (1.22)
N(2)-C(21)-C(22)	108.14 (1.08)	C(14)-C(5)-C(51)	116.87 (1.16)	C(7M)-C(74)-C(73)	119.91 (1.31)
C(21)-C(22)-C(23)	107.55 (1.23)	C(21)-C(5)-C(51)	117.00 (1.11)	C(7M)-C(74)-C(75)	121.49 (1.30)
C(22)-C(23)-C(24)	108.31 (1.23)	C(5)-C(51)-C(52)	120.24 (1.11)		
C(23)-C(24)-N(2)	109.91 (1.09)	C(5)-C(51)-C(56)	120.41 (1.20)	C(II)-C(8)-C(44)	123.32 (1.17)
C(24)-N(2)-C(21)	105.90 (1.06)	C(51)-C(52)-C(53)	118.49 (1.33)	C(11)-C(8)-C(81)	119.82 (1.08)
N(2)-C(21)-C(5)	125.90 (1.04)	C(52)-C(53)-C(54)	123.13 (1.41)	C(44)-C(8)-C(81)	116.77 (1.03)
C(5)-C(21)-C(22)	125.96 (1.17)	C(53)-C(54)-C(55)	117.57 (1.56)	C(8)-C(81)-C(82)	119.48 (1.02)
N(2)-C(24)-C(6)	125.72 (1.05)	C(54)-C(55)-C(56)	121.85 (1.51)	C(8)-C(81)-C(86)	122.23 (1.00)
C(6)-C(24)-C(23)	124.19 (1.14)	C(55)-C(56)-C(51)	119.51 (1.45)	C(81)-C(82)-C(83)	120.27 (1.14)
		C(56)-C(51)-C(52)	119.31 (1.33)	C(82)-C(83)-C(84)	120.56 (1.14)
		C(5M)-C(54)-C(53)	121.24 (1.48)	C(83)-C(84)-C(85)	117.37 (1.13)
		C(5M)-C(54)-C(55)	121.19 (1.53)	C(84)-C(85)-C(86)	122.68 (1.12)
				C(85)-C(86)-C(81)	120.68 (1.10)
				C(86)-C(81)-C(82)	118.28 (1.09)
				C(8M)-C(84)-C(83)	119.43 (1.13)
				C(8M)-C(84)-C(85)	123.05 (1.13)
CB(1)-CB(2)-CB(3)	120.34 (2.75)	CB(4)-CB(5)-CB(6)	119.65 (2.25)		
CB(2)-CB(3)-CB(4)	118.37 (2.66)	CB(5)-CB(6)-CB(1)	116.77 (2.24)		
CB(3)-CB(4)-CB(5)	119.74 (2.50)	CB(6)-CB(1)-CB(2)	124.87 (2.57)		

ᵃ Figures in parentheses here and in succeeding tables are estimated standard deviations. Benzene solvate carbons are labeled CB(1), CB(2), ..., CB(6).

value of its perpendicular displacement, in units of Å. A plus value represents a displacement on the oxo ligand side of the porphinato core. The molybdenum atom lies at 0.6389 (8) Å from the (4N) plane and at 0.7344 (8) Å from the (COR) mean plane of the porphine skeleton (see Table IV). The (4N) and the (COR) planes are nearly parallel, and the distance between these planes (0.09 Å) shows the domed character of the porphyrin. A slight doming was also observed in the oxo pentacoordinated derivatives TiO(OEP)[12] and VO(OEP)[13] where the metals are displaced 0.603 and 0.591 Å from the mean plane of the porphyrin core. Individually planar pyrrole rings (N1)–(N4) make dihedral angles of 3.9, 13.3, 5.2, and 13.9° with the (4N) plane. The overall geometry is also illustrated in Figure 3 by a stereoscopic view of the MoO(TTP) molecule.

We use C_α and C_β to denote the respective α- and β-carbon atoms of a pyrrole ring, C_m for methine carbon, and C_p for a phenyl carbon that is bonded to the core and give the following averaged bond lengths in the porphine skeleton: $N-C_\alpha$ = 1.392 (7), $C_\alpha-C_\beta$ = 1.431 (8), $C_\beta-C_\beta$ = 1.343 (12), $C_\alpha-C_m$
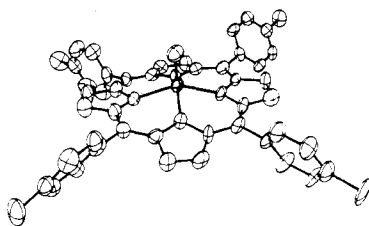
Figure 3. Stereoscopic view of the MoO(TTP) molecule.

Table III. Compared Mo=O Bond Lengths (Å) in Several Oxomolybdenum Compounds

compd	coord no. of Mo	Mo=O	ref
MoO(TCNE)(Pr$_2$NCS$_2$)$_2$	7	1.682 (4)	a
Mo$_2$O$_a$(PO$_2$)$_2$(C$_{10}$H$_{10}$N$_2$)$_2$	6	1.68 (2)	b
Mo$_2$O$_3$(S$_2$CSC$_3$H$_7$)$_4$	6	1.687 (12)	c
Mo$_2$S$_2$O$_2$(histidine)$_2$	6	1.676 (7)	d
Mo$_2$S$_2$O$_2$(cysteine)$_2$	6	1.62 (2)	e
Mo$_2$O$_4$(mercaptoethanol)(oxine)$_2$	6	1.693 (6)	f
[Mo$_2$O$_4$(Ac)(NCS)$_4$]$^{3-}$	6	1.683 (6)	g
MoO$_2$(Pr$_2$NCS$_2$)$_2$	6	1.695 (1)	h
Mo$_2$O$_3$(Pr$_2$NCS$_2$)$_4$	6	1.671 (4)	h
Mo$_2$O$_3$(TPP)$_2$	6	1.708 (3)	i
[MoO(H$_2$O)(CN)$_4$]$^{2-}$	6	1.668 (5)	j
[MoO(OH)(CN)$_4$]$^{2-}$	6	1.698 (7)	j
[Mo(diphos)$_2$(O)(OH)]$^+$	6	1.833 (5)	k
Mo$_2$O$_4$(Et$_2$NCS$_2$)$_2$	5	1.679 (2)	l
Mo$_2$O$_3$[S$_2$P(OC$_2$H$_5$)$_2$]$_4$	5	1.647 (14)	m
MoO(Pr$_2$NCS$_2$)$_2$	5	1.664 (8)	h
MoO(TTP)	5	1.656 (6)	this work

^{a} L. Ricard and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **10**, 217 (1974). ^{b} B. M. Gatehouse, E. K. Nunn, J. E. Guerchais, and R. Kergoat, *ibid.*, **12**, 23 (1976). ^{c} J. A. Zubieta and G. M. Maniloff, *ibid.*, **12**, 121 (1976). ^{d} B. Spivack and Z. Dori, *J. Chem. Soc., Dalton Trans.*, 1077 (1975). ^{e} D. H. Brown and J. A. D. Jeffreys, *ibid.*, 732 (1973). ^{f} J. I. Gelder, J. H. Enemark, G. Wolterman, D. A. Boston, and G. P. Haigh, *J. Am. Chem. Soc.*, **97**, 1616 (1975). ^{g} T. Gloviak and M. Sabat, *J. Cryst. Mol. Struct.*, **5**, 247 (1975). ^{h} L. Ricard, J. Estienne, P. Karagiannidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974). ^{i} Reference 2d. ^{j} P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **14**, 2035 (1975). ^{k} M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, **17**, 668 (1978). ^{l} L. Ricard, C. Martin, R. Wiest, and R. Weiss, *ibid.*, **14**, 2300 (1975). ^{m} J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 2281 (1969).

= 1.395 (7), C$_m$–C$_p$ = 1.503 (9) Å. The averaged bond angles are C$_\alpha$–N–C$_\alpha$ = 105.7 (6), N–C$_\alpha$–C$_\beta$ = 109.3 (4), N–C$_\alpha$–C$_m$ = 125.2 (4), C$_\alpha$–C$_\beta$–C$_\beta$ = 107.8 (5), C$_\alpha$–C$_m$–C$_\alpha$ = 124.4 (7), and C$_\alpha$–C$_m$–C$_p$ = 117.8 (4)°. The average of the 24 individually determined C–C bond distances in the peripheral tolyl rings is 1.386 (4) Å. On the other hand, the tolyl rings are tilted with respect to the plane of the three neighboring carbons of the bridge position between pyrroles; the tilted angles of the four tolyl rings Ph(5)–Ph(8) are 81.9, 56.1, 70.5, and 61.8°.

Finally, there are no unusual nonbonded contacts between molecules in the crystal. Intermolecular distances less than 3.60 Å and some selected intramolecular contacts are summarized in Table V.[10]

The Dichloro Compound (II). The asymmetric unit cell contains one molecule of the complex Mo(Cl)$_2$(TTP) and one benzene molecule of crystallization. Figure 4 shows a drawing of the Mo(Cl)$_2$(TTP) molecule, together with the atom labeling system used in the analysis; bond angles and lengths are listed in Table VI.

The molybdenum atom is hexacoordinated by the four pyrrole nitrogen atoms and two chlorine atoms. The two chlorine atoms are mutually trans with regard to the porphyrin ligand, and the Cl(1)–Mo–Cl(2) bond angle is equal to 178.4
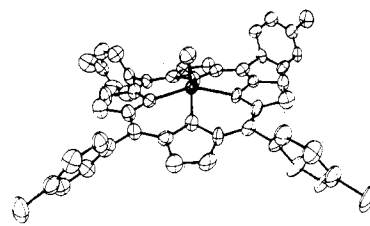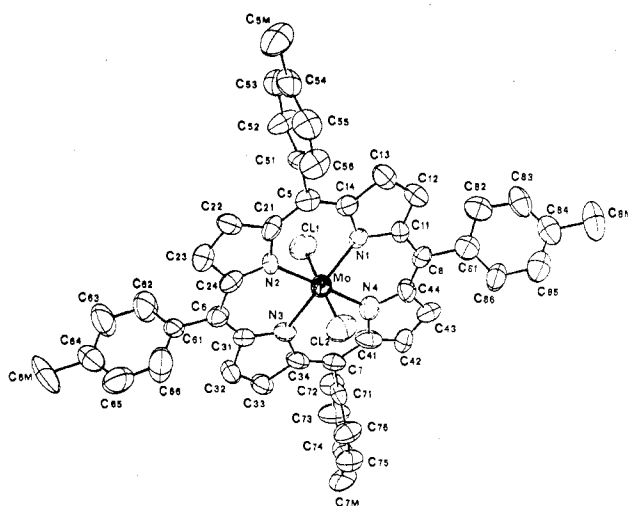

Figure 4. View of the Mo(Cl)$_2$(TTP) molecule (50% probability ellipsoids).

Figure 5. Diagram of the porphine skeleton as seen in Figure 4. The perpendicular displacements, in units of 0.1 Å, of the atoms from the (4N) plane replace the atomic symbols as carried in Figure 4.

(2)°. The four nitrogens are coplanar and the (4N) plane contains the molybdenum atom. The coplanarity of these atoms is also reflected in the angles at the molybdenum atom, with the N(1)–Mo–N(3) and N(2)–Mo–N(4) angles of 178.4 (5) and 179.3 (5)°, respectively. Moreover, the porphine skeleton is planar within experimental error and contains the molybdenum atom. Atomic distances from mean planes are summarized in Table VII. The (4N) and (COR) planes are nearly parallel, making a small dihedral angle of 1.5°. Figure 5 displays the atomic deviations, in units of 0.1 Å, from the (4N) plane. As expected, individual pyrrole rings are quite planar. The (N1)–(N4) pyrrole planes make dihedral angles of 2.9, 3.7, 1.6, and 4.2°, respectively, with the (4N) plane. Also small angles of 4–5° occur between adjacent pyrroles (Table VII). The departures from planarity observed here are closely similar to those found in so-called planar metalloporphyrins.[14] As currently observed, the tolyl rings are tilted with respect to the porphinato core; the tilted angles are 83.9,

Table IV. Least-Squares Planes for MoO(TTP)

Planes and Deviations (Å)

(COR): N(1), C(11)–C(14), N(2), C(21)–C(24), N(3),
C(31)–C(34), N(4), C(41)–C(44), C(5), C(6), C(7), C(8)

N(1)	0.156 (9)	C(32)	0.246 (14)
C(11)	0.221 (14)	C(33)	0.116 (14)
C(12)	0.292 (14)	C(34)	0.054 (12)
C(13)	0.167 (14)	N(4)	0.076 (9)
C(14)	0.084 (13)	C(41)	−0.152 (13)
N(2)	0.048 (9)	C(42)	−0.460 (13)
C(21)	−0.181 (12)	C(43)	−0.413 (13)
C(22)	−0.486 (13)	C(44)	−0.069 (12)
C(23)	−0.381 (13)	C(5)	−0.132 (10)
C(24)	−0.015 (12)	C(6)	0.143 (10)
N(3)	0.106 (9)	C(7)	−0.079 (10)
C(31)	0.196 (12)	C(8)	0.121 (10)
		Mo	0.7344 (8)^a

(4N): N(1), N(2), N(3), N(4)

N(1)	0.034 (9)	N(4)	−0.032 (9)
N(2)	−0.034 (9)	Mo	0.6389 (8)^a
N(3)	0.035 (9)		

(N1): N(1), C(11)–C(14)

N(1)	0.012 (9)	C(14)	−0.011 (13)
C(11)	−0.028 (14)	C(5)	−0.120 (9)^a
C(12)	0.024 (15)	C(8)	−0.207 (9)^a
C(13)	−0.007 (14)		

(N2): N(2), C(21)–C(24)

N(2)	0.017 (9)	C(24)	−0.022 (11)
C(21)	−0.024 (12)	C(5)	−0.080 (9)^a
C(22)	0.012 (13)	C(6)	0.007 (9)^a
C(23)	0.009 (13)		

(N3): N(3), C(31)–C(34)

N(3)	−0.004 (9)	C(34)	−0.004 (12)
C(31)	0.013 (11)	C(6)	0.147 (9)^a
C(32)	−0.018 (14)	C(7)	0.021 (9)^a
C(33)	0.015 (14)		

(N4): N(4), C(41)–C(44)

N(4)	−0.004 (9)	C(44)	0.005 (12)
C(41)	0.007 (12)	C(7)	0.032 (9)^a
C(42)	−0.005 (13)	C(8)	0.050 (9)^a
C(43)	−0.001 (13)		

(Ph5): C(51)–C(56)

C(51)	−0.002 (13)	C(55)	0.010 (18)
C(52)	0.015 (13)	C(56)	−0.011 (16)
C(53)	−0.026 (16)	C(5)	0.046 (10)^a
C(54)	0.009 (14)	C(5M)	0.052 (17)^a

(Ph6): C(61)–C(66)

C(61)	0.008 (10)	C(65)	−0.002 (11)
C(62)	−0.009 (11)	C(66)	−0.002 (10)
C(63)	0.004 (11)	C(6)	−0.037 (10)^a
C(64)	0.002 (11)	C(6M)	−0.068 (13)^a

(Ph7): C(71)–C(76)

C(71)	−0.001 (13)	C(75)	0.000 (14)
C(72)	−0.004 (14)	C(76)	0.003 (13)
C(73)	0.009 (15)	C(7)	−0.032 (10)^a
C(74)	−0.007 (14)	C(7M)	−0.039 (16)^a

(Ph8): C(81)–C(86)

C(81)	0.022 (12)	C(85)	0.009 (12)
C(82)	−0.006 (12)	C(86)	−0.021 (11)
C(83)	−0.009 (13)	C(8)	0.128 (10)^a
C(84)	0.006 (12)	C(8M)	0.120 (13)^a

Equations^b

plane	A	B	C	D	plane	A	B	C	D
(COR)	0.0269	−0.9995	−0.0185	−2.1709	(Ph5)	0.6314	−0.0043	−0.7755	1.2739
(4N)	0.0322	−0.9990	−0.0315	−2.0737	(Ph6)	−0.5834	−0.6335	−0.5083	−4.8821
(N1)	0.0938	−0.9938	−0.0596	−1.8629	(Ph7)	0.5562	−0.3817	−0.7382	0.5336
(N2)	−0.2506	0.9673	−0.0403	0.4896	(Ph8)	−0.5681	0.5751	−0.5886	−2.8276
(N3)	0.0417	0.9989	−0.0216	2.3744					
(N4)	−0.2093	−0.9771	−0.0372	−2.6660					

Angles (deg) between the Planes

(4N)–(COR)	0.8	(4N)–(N3)	5.2	(N1)–(N2)	10.8	(N1)–(N3)	9.1
(4N)–(N1)	3.9	(4N)–(N4)	13.9	(N2)–(N3)	16.9	(N2)–(N4)	17.0
(4N)–(N2)	13.3			(N3)–(N4)	10.3		
				(N4)–(N1)	17.5		

^{a} Atoms not included in the calculation. ^{b} All planes are unweighted and in the form $AX + BY + CZ - D = 0$ referring to the axial system a, b, c^*.
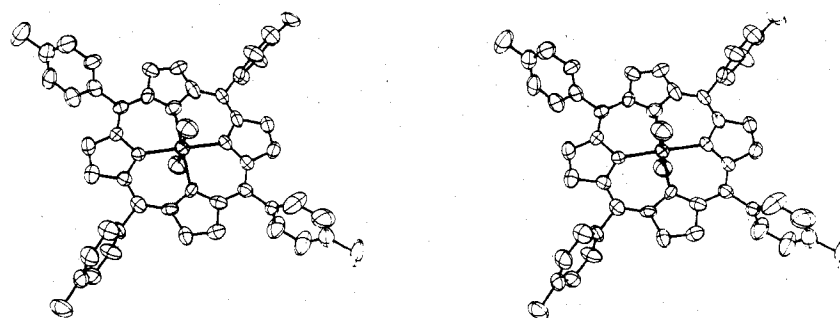
Figure 6. Stereoscopic drawing of the Mo(Cl)$_2$(TTP) molecule.

78.3, 85.0, and 65.5°. The individual C–C bond distances in the four structurally independent tolyl rings average to 1.400 (5) Å. A stereoscopic view of the complex is shown in Figure 6.

The average bond lengths of a given chemical type in the porphinato core are N–C$_\alpha$ = 1.385 (6), C$_\alpha$–C$_\beta$ = 1.447 (7), C$_\beta$–C$_\beta$ = 1.376 (11), C$_\alpha$–C$_m$ = 1.402 (7), and C$_m$–C$_p$ = 1.506

(11) Å. Average bond angles of a chemical type are C$_\alpha$–N–C$_\alpha$ = 107.8 (6), N–C$_\alpha$–C$_\beta$ = 108.7 (4), N–C$_\alpha$–C$_m$ = 125.7 (4), C$_\alpha$–C$_\beta$–C$_\beta$ = 107.3 (4), C$_\alpha$–C$_m$–C$_\alpha$ = 126.3 (7), and C$_\alpha$–C$_m$–C$_p$ = 116.8 (4)°.

Although the chlorine atoms are chemically equivalent, the two Mo–Cl distances appear to be somewhat different. Thus the Mo–Cl(1) distance of 2.347 (4) Å is longer than the

Table VI. Molecular Bond Lengths and Angles in Mo(Cl)$_2$(TTP)·C$_6$H$_6$

Bond Lengths (Å)

Mo–Cl(1)	2.347 (4)	N(4)–C(41)	1.404 (20)	C(6)–C(24)	1.406 (17)	C(8)–C(11)	1.385 (17)
Mo–Cl(2)	2.276 (4)	C(41)–C(42)	1.388 (22)	C(6)–C(31)	1.405 (18)	C(8)–C(44)	1.430 (17)
Mo–N(1)	2.045 (9)	C(42)–C(43)	1.366 (19)	C(6)–C(61)	1.461 (17)	C(8)–C(81)	1.523 (18)
Mo–N(2)	2.087 (10)	C(43)–C(44)	1.455 (20)	C(61)–C(62)	1.368 (21)	C(81)–C(82)	1.440 (22)
Mo–N(3)	2.067 (10)	C(44)–N(4)	1.377 (16)	C(62)–C(63)	1.438 (23)	C(82)–C(83)	1.416 (21)
Mo–N(4)	2.097 (11)			C(63)–C(64)	1.427 (26)	C(83)–C(84)	1.379 (25)
		C(5)–C(14)	1.374 (18)	C(64)–C(65)	1.354 (28)	C(84)–C(85)	1.389 (26)
N(1)–C(11)	1.392 (15)	C(5)–C(21)	1.413 (16)	C(65)–C(66)	1.423 (29)	C(85)–C(86)	1.438 (21)
C(11)–C(12)	1.425 (18)	C(5)–C(51)	1.533 (19)	C(66)–C(61)	1.388 (22)	C(86)–C(81)	1.406 (20)
C(12)–C(13)	1.389 (21)	C(51)–C(52)	1.355 (21)	C(64)–C(6M)	1.561 (23)	C(84)–C(8M)	1.512 (24)
C(13)–C(14)	1.460 (18)	C(52)–C(53)	1.435 (22)				
C(14)–N(1)	1.397 (17)	C(53)–C(54)	1.380 (21)	C(7)–C(34)	1.375 (19)	CB(1)–CB(2)	1.321 (45)
		C(54)–C(55)	1.370 (24)	C(7)–C(41)	1.432 (18)	CB(2)–CB(3)	1.319 (43)
N(2)–C(21)	1.382 (16)	C(55)–C(56)	1.388 (24)	C(7)–C(71)	1.508 (19)	CB(3)–CB(4)	1.421 (36)
C(21)–C(22)	1.443 (18)	C(56)–C(51)	1.421 (20)	C(71)–C(72)	1.390 (19)	CB(4)–CB(5)	1.355 (40)
C(22)–C(23)	1.407 (18)	C(54)–C(5M)	1.505 (23)	C(72)–C(73)	1.419 (24)	CB(5)–CB(6)	1.455 (46)
C(23)–C(24)	1.449 (20)			C(73)–C(74)	1.411 (23)	CB(6)–CB(1)	1.366 (48)
C(24)–N(2)	1.361 (15)			C(74)–C(75)	1.386 (20)		
				C(75)–C(76)	1.396 (24)		
N(3)–C(31)	1.377 (16)			C(76)–C(71)	1.400 (23)		
C(31)–C(32)	1.470 (18)			C(74)–C(7M)	1.514 (19)		
C(32)–C(33)	1.342 (20)						
C(33)–C(34)	1.489 (18)						
C(34)–N(3)	1.394 (18)						

Bond Angles (deg)

Cl(1)–Mo–Cl(2)	178.44 (20)	Mo–N(3)–C(31)	125.69 (66)	C(24)–C(6)–C(31)	122.98 (1.16)
Cl(1)–Mo–N(1)	90.79 (28)	Mo–N(3)–C(34)	125.22 (67)	C(24)–C(6)–C(61)	119.55 (1.11)
Cl(1)–Mo–N(2)	91.60 (27)	N(3)–C(31)–C(32)	108.21 (1.06)	C(31)–C(6)–C(61)	117.21 (1.12)
Cl(1)–Mo–N(3)	87.67 (29)	C(31)–C(32)–C(33)	107.85 (1.17)	C(6)–C(61)–C(62)	122.51 (1.25)
Cl(1)–Mo–N(4)	88.33 (28)	C(32)–C(33)–C(34)	108.08 (1.18)	C(6)–C(61)–C(66)	118.51 (1.31)
Cl(2)–Mo–N(1)	89.81 (28)	C(33)–C(34)–N(3)	106.60 (1.07)	C(61)–C(62)–C(63)	120.69 (1.43)
Cl(2)–Mo–N(2)	89.83 (27)	C(34)–N(3)–C(31)	109.09 (1.10)	C(62)–C(63)–C(64)	118.24 (1.52)
Cl(2)–Mo–N(3)	91.73 (29)	N(3)–C(31)–C(6)	127.92 (1.12)	C(63)–C(64)–C(65)	121.07 (1.77)
Cl(2)–Mo–N(4)	90.23 (29)	C(6)–C(31)–C(32)	123.61 (1.16)	C(64)–C(65)–C(66)	118.56 (1.78)
		N(3)–C(34)–C(7)	126.36 (1.15)	C(65)–C(66)–C(61)	122.39 (1.65)
N(1)–Mo–N(2)	90.66 (39)	C(7)–C(34)–C(33)	126.58 (1.21)	C(66)–C(61)–C(62)	118.87 (1.47)
N(2)–Mo–N(3)	89.47 (40)			C(6M)–C(64)–C(63)	117.28 (1.51)
N(3)–Mo–N(4)	89.90 (42)	Mo–N(4)–C(41)	128.20 (68)	C(6M)–C(64)–C(65)	121.65 (1.70)
N(4)–Mo–N(1)	89.97 (40)	Mo–N(4)–C(44)	126.17 (66)		
N(1)–Mo–N(3)	178.46 (48)	N(4)–C(41)–C(42)	110.25 (1.15)	C(34)–C(7)–C(41)	129.58 (1.26)
N(2)–Mo–N(4)	179.37 (47)	C(41)–C(42)–C(43)	108.94 (1.26)	C(34)–C(7)–C(71)	115.89 (1.15)
		C(42)–C(43)–C(44)	105.62 (1.18)	C(41)–C(7)–C(71)	114.45 (1.14)
Mo–N(1)–C(11)	126.73 (60)	C(43)–C(44)–N(4)	109.83 (1.09)	C(7)–C(71)–C(72)	118.63 (1.19)
Mo–N(1)–C(14)	126.48 (63)	C(44)–N(4)–C(41)	105.32 (1.12)	C(7)–C(71)–C(76)	120.47 (1.22)
N(1)–C(11)–C(12)	108.42 (1.03)	N(4)–C(41)–C(7)	120.47 (1.13)	C(71)–C(72)–C(73)	118.43 (1.35)
C(11)–C(12)–C(13)	110.46 (1.16)	C(7)–C(41)–C(42)	129.24 (1.26)	C(72)–C(73)–C(74)	120.67 (1.36)
C(12)–C(13)–C(14)	103.78 (1.16)	N(4)–C(44)–C(8)	123.95 (1.08)	C(73)–C(74)–C(75)	119.53 (1.39)
C(13)–C(14)–N(1)	110.69 (1.07)	C(8)–C(44)–C(43)	126.06 (1.16)	C(74)–C(75)–C(76)	120.13 (1.37)
C(14)–N(1)–C(11)	106.64 (1.01)			C(75)–C(76)–C(71)	120.43 (1.36)
N(1)–C(11)–C(8)	125.52 (1.03)	C(14)–C(5)–C(21)	125.72 (1.14)	C(76)–C(71)–C(72)	120.79 (1.34)
C(8)–C(11)–C(12)	126.03 (1.14)	C(14)–C(5)–C(51)	118.77 (1.14)	C(7M)–C(74)–C(73)	120.24 (1.33)
N(1)–C(14)–C(5)	125.81 (1.09)	C(21)–C(5)–C(51)	115.51 (1.07)	C(7M)–C(74)–C(75)	120.22 (1.31)
C(5)–C(14)–C(13)	123.41 (1.19)	C(5)–C(51)–C(52)	118.96 (1.21)		
		C(5)–C(51)–C(56)	118.55 (1.19)	C(11)–C(8)–C(44)	127.04 (1.13)
Mo–N(2)–C(21)	123.77 (58)	C(51)–C(52)–C(53)	117.94 (1.32)	C(11)–C(8)–C(81)	117.88 (1.11)
Mo–N(2)–C(24)	125.70 (62)	C(52)–C(53)–C(54)	120.97 (1.36)	C(44)–C(8)–C(81)	115.07 (1.13)
N(2)–C(21)–C(22)	106.62 (99)	C(53)–C(54)–C(55)	118.71 (1.37)	C(8)–C(81)–C(82)	119.79 (1.19)
C(21)–C(22)–C(23)	108.65 (1.10)	C(54)–C(55)–C(56)	123.00 (1.40)	C(8)–C(81)–C(86)	117.96 (1.18)
C(22)–C(23)–C(24)	105.34 (1.11)	C(55)–C(56)–C(51)	116.85 (1.31)	C(81)–C(82)–C(83)	117.42 (1.34)
C(23)–C(24)–N(2)	108.98 (1.05)	C(56)–C(51)–C(52)	122.41 (1.36)	C(82)–C(83)–C(84)	121.41 (1.46)
C(24)–N(2)–C(21)	110.40 (1.01)	C(5M)–C(54)–C(53)	119.35 (1.36)	C(83)–C(84)–C(85)	120.41 (1.51)
N(2)–C(21)–C(5)	127.46 (1.03)	C(5M)–C(54)–C(55)	121.63 (1.36)	C(84)–C(85)–C(86)	121.66 (1.45)
C(5)–C(21)–C(22)	125.90 (1.11)			C(85)–C(86)–C(81)	116.72 (1.35)
N(2)–C(24)–C(6)	128.01 (1.08)			C(86)–C(81)–C(82)	122.18 (1.33)
C(6)–C(24)–C(23)	123.01 (1.16)			C(8M)–C(84)–C(83)	120.14 (1.51)
				C(8M)–C(84)–C(85)	119.31 (1.53)
				CB(1)–CB(2)–CB(3)	127.85 (2.77)
				CB(2)–CB(3)–CB(4)	114.78 (2.39)
				CB(3)–CB(4)–CB(5)	123.23 (2.40)
				CB(4)–CB(5)–CB(6)	115.70 (2.61)
				CB(5)–CB(6)–CB(1)	120.62 (2.84)
				CB(6)–CB(1)–CB(2)	117.20 (2.95)

Mo–Cl(2) distance of 2.276 (4) Å. We cannot offer at this point a reasonable explanation. Moreover, there are no unusual contacts around chlorine atoms. (See Table VIII.[10]) In spite of this, our opinion is that the averaged value of 2.311 Å is the most appropriate value for describing the Mo–Cl distance in this compound. For comparison a longer Mo–Cl

distance, 2.388 (2) Å, was determined in Mo(sal-NCH$_3$)$_2$Cl$_2$ where the chlorine atoms are also in a trans arrangement.[15] The four Mo–N bond lengths are not significantly different within experimental error and average to 2.074 (6) Å. Although substantially shorter, this Mo–N bond length compares well with those of 2.096 (4) Å found in MoO$_4$(TTP)[1] and

Table VII. Mean Planes for $Mo(Cl)_2(TTP)$

Planes and Deviations (Å)

(COR): N(1), C(11)–C(14), N(2), C(21)–C(24), N(3),
C(31)–C(34), N(4), C(41)–C(44), C(5), C(6), C(7), C(8)

N(1)	−0.046 (10)	C(33)	−0.007 (14)
C(11)	0.004 (12)	C(34)	0.065 (14)
C(12)	0.047 (14)	N(4)	0.056 (11)
C(13)	0.021 (14)	C(41)	0.020 (16)
C(14)	−0.042 (13)	C(42)	−0.064 (14)
N(2)	−0.037 (10)	C(43)	−0.056 (14)
C(21)	−0.014 (12)	C(44)	−0.012 (14)
C(22)	0.056 (13)	C(5)	−0.022 (12)
C(23)	0.046 (14)	C(6)	−0.005 (13)
C(24)	−0.006 (13)	C(7)	0.022 (13)
N(3)	0.012 (11)	C(8)	0.053 (12)
C(31)	−0.042 (13)	Mo	0.010 (1)[a]
C(32)	−0.011 (13)		

(4N): N(1), N(2), N(3), N(4)

N(1)	−0.012 (10)	N(4)	0.014 (11)
N(2)	0.012 (10)	Mo	0.014 (1)[a]
N(3)	−0.014 (11)		

(N1): N(1), C(11)–C(14)

N(1)	0.001 (10)	C(14)	−0.002 (13)
C(11)	−0.001 (12)	C(5)	0.059 (12)[a]
C(12)	0.000 (14)	C(8)	0.035 (12)[a]
C(13)	0.001 (14)		

(N2): N(2), C(21)–C(24)

N(2)	0.002 (10)	C(24)	0.000 (13)
C(21)	−0.006 (12)	C(5)	0.005 (12)[a]
C(22)	0.006 (13)	C(6)	0.016 (12)[a]
C(23)	−0.005 (13)		

(N3): N(3), C(31)–C(34)

N(3)	−0.002 (11)	C(34)	0.017 (14)
C(31)	−0.008 (13)	C(6)	0.073 (12)[a]
C(32)	0.021 (13)	C(7)	−0.077 (13)[a]
C(33)	−0.024 (14)		

(N4): N(4), C(41)–C(44)

N(4)	0.004 (11)	C(44)	−0.012 (14)
C(41)	0.002 (16)	C(7)	−0.036 (13)[a]
C(42)	−0.009 (14)	C(8)	0.042 (12)[a]
C(43)	0.012 (14)		

(Ph5): C(51)–C(56)

C(51)	−0.011 (13)	C(55)	−0.013 (13)
C(52)	0.003 (14)	C(56)	0.019 (15)
C(53)	0.002 (14)	C(5)	0.013 (12)[a]
C(54)	0.002 (15)	C(5M)	−0.123 (17)[a]

(Ph6): C(61)–C(66)

C(61)	0.005 (12)	C(65)	−0.014 (21)
C(62)	0.003 (18)	C(66)	−0.009 (19)
C(63)	−0.023 (19)	C(6)	0.104 (12)[a]
C(64)	0.022 (17)	C(6M)	0.099 (22)[a]

(Ph7): C(71)–C(76)

C(71)	−0.003 (12)	C(75)	0.007 (15)
C(72)	0.002 (14)	C(76)	−0.001 (15)
C(73)	0.003 (16)	C(7)	−0.098 (12)[a]
C(74)	−0.006 (13)	C(7M)	−0.058 (16)[a]

(Ph8): C(81)–C(86)

C(81)	0.018 (15)	C(85)	−0.025 (17)
C(82)	−0.022 (15)	C(86)	0.001 (15)
C(83)	0.006 (17)	C(8)	0.010 (12)[a]
C(84)	0.020 (18)	C(8M)	−0.010 (20)[a]

Equations[b]

plane	A	B	C	D	plane	A	B	C	D
(COR)	0.494	−0.758	−0.427	1.325	(Ph5)	0.694	0.700	−0.165	8.588
(4N)	0.501	−0.766	−0.402	1.349	(Ph6)	−0.450	0.436	−0.778	−2.656
(N1)	0.458	−0.779	−0.427	0.812	(Ph7)	0.749	0.580	−0.318	8.919
(N2)	0.503	−0.732	−0.458	1.375	(Ph8)	−0.571	0.533	−0.623	−2.764
(N3)	0.477	−0.781	−0.402	1.127					
(N4)	0.513	−0.723	−0.461	1.777					

Angles (deg) between the Planes

(4N)–(COR)	1.5	(4N)–(N1)	2.9	(N1)–(N2)	4.1	(N1)–(N3)	1.8
		(4N)–(N2)	3.7	(N2)–(N3)	4.5	(N2)–(N4)	0.8
		(4N)–(N3)	1.6	(N3)–(N4)	5.1		
		(4N)–(N4)	4.2	(N4)–(N1)	4.9		

[a] Atoms not included in the calculation. [b] All planes are unweighted and in the form $AX + BY + CZ - D = 0$ referring to the axial system a, b, c^*.

2.094 (3) Å in $Mo_2O_3(TPP)_2$.[2d] In contrast, the significantly longer distance of 2.110 (6) Å in the above-described MoO(TTP) complex results from the severe out-of-plane displacement (0.73 Å) of the molybdenum atom.

Intermolecular distances and some pertinent intramolecular distances are listed in Table VIII.[10] There are no unusual intermolecular contacts. The shortest contact is 3.41 Å between the Cl(1) chlorine atom of one molecule and the C(65) phenyl carbon of an adjacent molecule. Benzene solvate provides only weak contacts with neighboring molecules upward of 3.72 Å.

Compared Results and Discussion. It is well-known that the porphyrinate anion forms chelates with cations of notably varied size and electronic structure. The porphine skeleton is subjected to varying radial strain in its mean plane when cations of very different ionic (or covalent) radius are complexed. Such strain has been analyzed in the skeletal bond lengths and angles.[16] A useful parameter for discussion is the radius of the central core of the porphine skeleton, C_t–N, the distance from the center to the porphine nitrogen atoms. It

has been estimated that the radial strain in the core of a metalloporphyrin is minimized for a C_t–N radius of 2.01 Å.[17]

In MoO(TTP) the radius of the central core of the porphine skeleton is C_t–N = 2.011 Å, smaller than the Mo–N bond length of 2.110 (6) Å because the molybdenum lies 0.73 Å out-of-plane toward the apical oxygen atom. In $Mo(Cl)_2(TTP)$ the radius coincides with the complexing bond length C_t–N = Mo–N = 2.074 (6) Å because the molybdenum is centered in the mean plane. This last radius, while not as large as the 2.098 Å value[18] in planar $Sn(Cl)_2(TPP)$, still corresponds to an expanded core.

Averaged bond lengths and angles in the cores of the MoO(TTP) and $Mo(Cl)_2(TTP)$ molecules are compared in Table IX with those of metalloporphyrins in which extreme values of the complexing M–N bond lengths are utilized. It will be noted that the increase in the C_t–N radius is attended by a small compression of the N–C_α bond and by extensions of the C_β–C_β and C_α–C_m bonds. There are also some interesting trends in bond angles, particularly the C_α–N–C_α and C_α–C_m–C_α angles. These angles increase with increasing C_t–N

Table IX. Averaged Parameters of the Porphine Skeleton in Metalloporphyrins as a Function of the Radius of the Central Core, C_t-N

	Ni(DEUT)^a	MoO(TTP)	Mo(Cl)$_2^-$ (TTP)	Sn(Cl)$_2^-$ (TPP)^b
Distances (Å)				
C_t-N	1.960	2.011	2.074	2.098
M-N	1.960 (4)	2.110 (6)	2.074 (6)	2.098 (2)
$\Delta P_M{}^c$	0.0	0.73	0.0	0.0
N-C_α	1.383 (3)	1.392 (7)	1.385 (6)	1.370 (2)
C_β-C_β	1.350 (5)	1.343 (12)	1.376 (11)	1.380 (3)
C_α-C_m	1.375 (4)	1.395 (7)	1.402 (7)	1.407 (2)
Angles (deg)				
C_α-N-C_α	104.5 (6)	105.7 (6)	107.8 (6)	109.2 (2)
C_α-C_m-C_α	123.9 (4)	124.4 (7)	126.3 (7)	126.4 (2)
N-C_α-C_β	110.0 (5)	109.3 (4)	108.7 (4)	108.2 (2)

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radius. Hoard has noted this tendency and points out[19] that an increase in the C_α-N-C_α angle is conducive to stronger complexing, but the amount of expansion of this angle is limited by the need to keep the N-C_α-C_β angle as large as possible. As a conclusion, the Mo(IV) ion is possibly more strongly complexed in Mo(Cl)$_2$(TTP) than in MoO(TTP).

Registry No. I, 69501-68-4; II, 64024-41-5; MoO(Cl)(TTP)·HCl, 69484-02-2; MoOCl$_3$, 13814-74-9.

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Structure of
Bis(*tert*-butyl isocyanide)(*meso*-tetraphenylporphyrinato)iron(II)−Bis(toluene)

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The structure of bis(*tert*-butyl isocyanide)(*meso*-tetraphenylporphyrinato)iron(II)−bis(toluene) has been determined by three-dimensional, single-crystal X-ray diffraction methods. The material crystallizes with four formula units in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions $a = 22.113$ (7) Å, $b = 12.581$ (4) Å, $c = 19.455$ (8) Å, $\beta = 94.55$ (1)°, and $V = 5396$ Å^3 at −150 °C. The structure described by 408 variable parameters has been refined by full-matrix, least-squares techniques to values of the agreement index R (on F^2, 8186 data including $F_o{}^2 < 0$) of 0.071 corresponding to a value of R (on F, 6747 data having $F_o{}^2 > 3\sigma(F_o{}^2)$) of 0.049. The geometry about the iron atom is approximately tetragonal with Fe−N(porph) separations of 2.000 (1), 2.010 (2), 2.005 (2), and 2.004 (2) Å and with Fe−C(*t*-BuNC) separations of 1.901 (3) and 1.900 (3) Å. Although there are large deviations of the Fe−C−N−C moiety of the Fe-*t*-BuNC groups from linearity (Fe−C−N angles, 168.1 (2) and 169.9 (2)°; CNC angles, 159.1 (3) and 165.2 (3)°), we conclude, from crystal packing considerations, that the isocyanide geometry is essentially linear. Such a linear geometry may be expected in the corresponding isocyanide adducts of hemoproteins.

Introduction

Of the small molecules, L = O_2, CO, NO, and RNC which bind to ferrous hemoproteins,[1] X-ray crystal structures of simple Fe^{II}(porphyrinato)(L)(base) complexes are available for all except isocyanide, L = RNC.[2-5] In a classic paper on the bonding of these ligands to the heme center,[6] Pauling predicted an angular iron–dioxygen geometry, I, and a linear iron–carbonyl geometry, II. These have been strongly supported by the structures of model complexes.[2-4] Geometry I for dioxygen is consistent with the present structure of
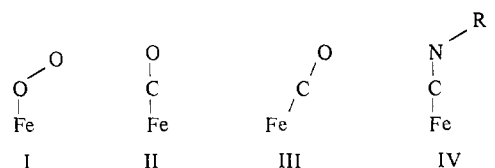
oxymyoglobin.[7,8] The apparently bent geometry claimed[9-11] for several carbonyl hemoglobin compounds[9-12] is probably better interpreted as a tilted but linear geometry, III.[4,13] An angular geometry has been observed in the structure of the