$(TMSO)_2Cl_2]_2{}^{36}$ to $+6.3$ cm^{-1} in $[Cu(dmg)Cl_2]_2$.[30] The relationship between J and φ/r_o is essentially linear for the chloride-bridged dimers, but the range of J and φ/r_o is more limited than that of the sulfur-bridged compounds and curvature is anticipated.

Since the angle at the bridge determines the sign of the exchange-coupling constant, we may expect that the line in Figure 2 will reach a maximum value at some larger value of φ/r_o and then begin to decrease with an increase in φ/r_o. There are data which support this view. The compounds Cu(dimethyl sulfoxide)$_2$Cl$_2$,[37,38] Cu(H$_2$O)(caffeine)Cl$_2$,[39,40] Cu(imidazole)$_2$Cl$_2$,[40,42] and Cu[2-(2-(methylamino)ethyl)pyridine]-Cl$_2$[32,40,42] have single-chloride-bridged chain structures with angles which range from 113° in Cu(MAEP)Cl$_2$[43] to 144° in Cu(Me$_2$SO)$_2$Cl$_2$.[37] Except for Cu(imidazole)$_2$Cl$_2$, which undergoes long-range ordering below 7.7 K,[40] the exchange-coupling constant decreases (from $+1.48$ cm^{-1} for Cu(MAEP)Cl$_2$[32,40] to -6.1 cm^{-1} for Cu(Me$_2$SO)$_2$Cl$_2$[38]) as φ/r_o increases. Should examples of copper complexes with larger angles be found, it is likely that the exchange coupling constants will be negative.

The results of this study have shown that sulfur donor bridges between copper ions in dimers and chains transmit superexchange interaction and that these interactions are large even though long bonds are involved in the bridged units. In addition it appears that the angle at the bridge and the length of the bridge bonds determine the nature of the exchange coupling in a systematic way.

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Molybdenum–Porphyrin Derivatives: Synthesis and X-ray Crystal Structure of Bis(phenyldiazo)(*meso*-tetra-*p*-tolylporphyrinato)molybdenum(IV) Phenylhydrazine Solvate, Mo(N₂C₆H₅)₂(TTP)·C₆H₅NHNH₂

JOCELYNE COLIN, GRAHAM BUTLER, and RAYMOND WEISS*

Reaction of phenylhydrazine with the dichloromolydbenum(IV) porphyrin complex MoCl$_2$(TTP) leads to the corresponding diazomolybdenum complex Mo(N$_2$C$_6$H$_5$)$_2$(TTP) (TTP is the dianion of the *meso*-tetratolylporphyrin). The molecular structure of this complex has been determined by X-ray diffraction techniques. The molybdenum is hexacoordinated with the diazo ligands in trans position with respect to the porphyrin plane. The complex is located on a crystallographic inversion center and thus presents C_i molecular symmetry. The geometry of the aryldiazo group is intermediate between singly and doubly bent. Some relevant metrical parameters are Mo–N(diazo) = 2.060 (5) Å, N–N = 1.133 (9) Å, N–C = 1.448 (12) Å, M–N–N = 149.1 (9)°, and N–N–C = 128.6 (9)°. Mo(N$_2$C$_6$H$_5$)$_2$(TTP) crystallizes in space group $C2/c$ with a = 26.734 (20) Å, b = 13.842 (9) Å, c = 17.883 (11) Å, β = 124.71 (9)°, and Z = 4. The structure determination and refinement were based on 2222 reflections with $I > 3\sigma(I)$. Final values of R and R_w are 0.078 and 0.098, respectively.

Introduction

Aryldiazo ligands may represent models for intermediates in chemical reduction of dinitrogen to ammonia or hydrazine.[2] They can adopt various coordination geometries: A–E.
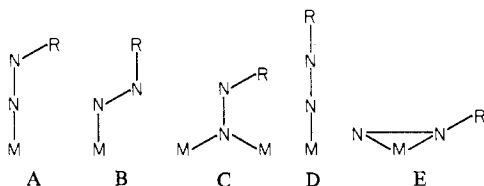
In the bonding modes A–C the aryldiazo ligand (obtained from diazonium salts[3,13] or aromatic hydrazines[4]) behaves as the isoelectronic nitrosyl group. Nitrosyl and aryldiazo ligands

have been compared structurally in almost identical coordination environments.[5] The bonding modes D[6] and E[7] were obtained with neutral RN$_2$ species. Recently, we reported the synthesis and structural study of a nitrosylmolybdenum por-

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Table I. Summary of Crystal Data and Intensity Collection

compd	$Mo(N_2C_6H_5)_2TTP \cdot C_6H_5NHNH_2$
formula	$C_{66}H_{54}N_{10}Mo$
fw	1083.2
space group	$C2/c$
cell const	
a, Å	26.734 (20)
b, Å	13.842 (9)
c, Å	17.883 (11)
α, deg	90
β, deg	124.71 (9)
γ, deg	90
V, Å^3	5440
Z	4
ρ(calcd), g cm^{-3}	1.332
cryst dimens, mm	0.14 × 0.18 × 0.22
radiatn	Mo Kα (λ = 0.7093 Å)
μ, cm^{-1}	2.94
data collectn method	θ–2θ
scan mode	flying step scan (step width = 0.05°)
ω scan speed, deg min^{-1}	1.92
scan range	0.70 + 0.34 tan θ
2θ limits, deg	4–55
measd reflctns	7752
obsd reflctns used, $I \geqslant 3\sigma(I)$	2222
p	0.06
final $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.078
final $R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/ \Sigma w\|F_o\|^2]^{1/2}$	0.098

Figure 1. Perspective drawing of the $Mo(N_2C_6H_5)_2(TTP)$ molecule as it exists in the crystal. The 30% probability vibration ellipsoids are shown. Tolyl groups have been omitted for clarity.

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.

phyrin derivative $Mo(NO)_2(TTP)$. In this compound the slightly bent NO groups are in cis position with respect to the porphyrinato skeleton. In order to compare the structures of the dinitrosyl and bis(aryldiazo) complexes, we have synthesized and studied the structure of $Mo(N_2C_6H_5)_2(TTP)$ from $MoCl_2(TTP)$ as starting material (TTP is the dianion of *meso*-tetratolylporphyrin).

Experimental Section

Synthesis and Characterization. All solvents were refluxed over calcium hydride for a minimum of 24 h and freshly distilled. Phenylhydrazine was analytical grade and was used without further purification. All reactions were carried out under dry argon by using Schlenk tubes. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer with Nujol mulls and visible spectra on a Beckman Acta III spectrophotometer in CH_2Cl_2 solutions. $MoCl_2(TTP)$ was prepared as previously described.[9]

A solution of $C_6H_5NHNH_2$ (200 μL = 2.0 mmol) in benzene (100 cm^3) was degassed and added to $MoCl_2(TTP)$ (300 mg, 0.36 mmol). This mixture was stirred overnight at room temperature. The solution turned from brown to red immediately, and a white solid began to precipitate. The infrared spectrum showed the precipitate to be $C_6H_5NHNH_3^+Cl^-$. Thin-layer chromatography indicated the resulting solution to be a mixture of two red products. The red filtrate was purified by passing it through a column packed with standardized Al_2O_3 and eluted with benzene. The first eluate was identified as the oxo species $MoO(TTP)$ in view of its IR spectrum ($\nu_{Mo=O}$ = 970 cm^{-1}).[9] The second product was eluted with CH_2Cl_2, evaporated to dryness, and dissolved in freshly degassed benzene. Pentane was added to yield crystals of $Mo(N_2C_6H_5)_2(TTP)\cdot C_6H_5NHNH_2$ after several days' storage at room temperature (208 mg, 55%). IR: 1595 cm^{-1} (N=N). Visible (λ, nm (log ε)): 431 (5.65), 554 (4.44), 593 (4.13), 635 (4.01).

X-ray Data Collection. Well-formed crystals suitable for an X-ray study were obtained at room temperature by slow diffusion of pentane
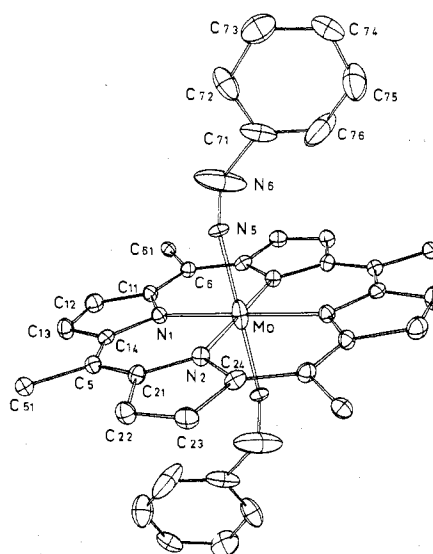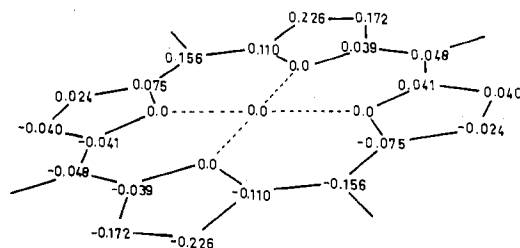
in a benzene solution of the complex containing traces of phenylhydrazine under argon. A crystal of 0.14 × 0.18 × 0.22 mm was sealed in a Lindemann glass capillary in a Vacuum Atmospheres inert-atmosphere box with a gas purifying system (<1 ppm oxygen) and mounted on a Philips PW1100 diffractometer. Space group ($C2/c$ or Cc) and 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 Mo Kα radiation. Crystal data are given in Table I. The diffraction data were collected at room temperature (20 ± 1 °C). The intensities of three standard reflections were measured every 90 min; the deviations were all within counting statistics. The intensity data were corrected by application of standard Lorentz and polarization factors. Absorption effects were neglected in view of the small crystal dimensions and linear absorption coefficient.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method in the space group $C2/c$. The Mo atom was located from a three-dimensional Patterson synthesis on an inversion center in the special position (0,0,0). Subsequent refinements and difference Fourier syntheses led to the location of all independent nonhydrogen atoms and confirmed the choice of space group.

The phenylhydrazine molecule of crystallization was found on a C_2 crystallographic axis passing through the nitrogen atom of the NH_2 group and the middle of two opposite C–C bonds of the ring. Thus, the NH group attached to the ring is disordered and occupies two positions which were refined by using an occupancy factor of $^1/_2$. The structure was refined by usual full-matrix, least-squares techniques. Calculations were performed on a PDP 11-60 computer using an Enraf-Nonius structure determination package. The aromatic hydrogen atoms were included as a fixed contribution, their position being idealized by assuming a trigonal-planar geometry and by using C–H distances of 1.00 Å. Each hydrogen atom was assigned an isotropic thermal parameter of 6 Å^2. All nonhydrogen atoms were refined by assuming anisotropic thermal motion to yield R = 0.078.

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Table II. Positional and Thermal Parameters for the Nonhydrogen Atoms of $Mo(N_2Ph)_2(TTP)\cdot C_6H_5NHNH_2$ [a]

atom	x [b]	y	z	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$
Mo	0.0000 (0)	0.0000 (0)	0.0000 (0)	0.00360 (3)	0.00656 (7)	0.00345 (4)	−0.00572 (8)	0.00218 (5)	0.0007 (1)
N(1)	−0.0675 (2)	−0.0705 (5)	−0.1159 (4)	0.0017 (1)	0.0038 (4)	0.0036 (3)	−0.0006 (4)	0.0023 (3)	−0.0002 (6)
N(2)	−0.0114 (3)	0.1198 (5)	−0.0786 (4)	0.0020 (1)	0.0039 (4)	0.0040 (3)	−0.0007 (4)	0.0032 (2)	0.0002 (6)
N(5)	0.0614 (2)	−0.0601 (5)	−0.0213 (4)	0.0021 (1)	0.0063 (5)	0.0058 (3)	0.0018 (4)	0.0053 (2)	−0.0010 (6)
N(6)	0.0940 (4)	−0.1208 (8)	−0.0080 (11)	0.0028 (2)	0.0084 (8)	0.0403 (14)	−0.0027 (7)	0.0137 (8)	−0.0134 (17)
N(7)	0.0390 (8)	0.2156 (16)	0.3154 (13)	0.0055 (5)	0.0138 (17)	0.0180 (13)	0.0066 (16)	0.0142 (10)	0.0156 (26)
N(8)	0.0000 (0)	0.1302 (11)	0.2500 (0)	0.0059 (3)	0.0087 (11)	0.0297 (13)	0.0000 (0)	0.0198 (8)	0.0000 (0)
C(11)	−0.0854 (3)	−0.1650 (6)	−0.1192 (5)	0.0016 (2)	0.0043 (5)	0.0039 (3)	−0.0014 (5)	0.0022 (3)	−0.0016 (7)
C(12)	−0.1340 (4)	−0.1852 (6)	−0.2120 (6)	0.0028 (2)	0.0046 (6)	0.0057 (4)	−0.0013 (6)	0.0041 (4)	−0.0019 (8)
C(13)	−0.1440 (4)	−0.1063 (6)	−0.2635 (5)	0.0030 (2)	0.0049 (6)	0.0038 (4)	−0.0011 (6)	0.0024 (4)	−0.0005 (8)
C(14)	−0.1016 (3)	−0.0330 (6)	−0.2035 (5)	0.0021 (2)	0.0058 (6)	0.0039 (3)	0.0015 (5)	0.0038 (3)	0.0000 (7)
C(21)	−0.0534 (3)	0.1296 (6)	−0.1712 (5)	0.0021 (2)	0.0048 (5)	0.0038 (3)	−0.0007 (5)	0.0037 (3)	0.0000 (7)
C(22)	−0.0506 (4)	0.2259 (6)	−0.1964 (5)	0.0023 (2)	0.0048 (5)	0.0044 (4)	−0.0006 (5)	0.0029 (4)	0.0009 (8)
C(23)	−0.0087 (4)	0.2737 (6)	−0.1216 (5)	0.0028 (2)	0.0036 (5)	0.0057 (4)	0.0003 (5)	0.0044 (4)	0.0015 (8)
C(24)	0.0172 (3)	0.2069 (6)	−0.0453 (5)	0.0024 (1)	0.0041 (5)	0.0052 (3)	−0.0006 (5)	0.0056 (3)	0.0004 (7)
C(5)	−0.0945 (3)	0.0597 (6)	−0.2289 (4)	0.0017 (1)	0.0045 (5)	0.0035 (3)	−0.0004 (5)	0.0032 (3)	0.0008 (7)
C(51)	−0.1345 (3)	0.0840 (6)	−0.3289 (5)	0.0019 (2)	0.0049 (5)	0.0041 (3)	−0.0001 (5)	0.0029 (3)	0.0003 (7)
C(52)	−0.1105 (3)	0.0985 (7)	−0.3784 (5)	0.0018 (2)	0.0068 (6)	0.0052 (3)	−0.0001 (5)	0.0042 (3)	0.0017 (8)
C(53)	−0.1486 (4)	0.1227 (7)	−0.4701 (5)	0.0033 (2)	0.0071 (7)	0.0050 (3)	−0.0006 (6)	0.0057 (3)	0.0020 (8)
C(54)	−0.2098 (3)	0.1311 (6)	−0.5140 (5)	0.0026 (2)	0.0052 (5)	0.0046 (3)	−0.0004 (5)	0.0047 (3)	−0.0002 (7)
C(55)	−0.2335 (4)	0.1164 (7)	−0.4655 (5)	0.0018 (2)	0.0081 (7)	0.0048 (4)	0.0017 (6)	0.0025 (4)	0.0017 (9)
C(56)	−0.1974 (3)	0.0924 (8)	−0.3742 (5)	0.0024 (2)	0.0092 (7)	0.0054 (3)	0.0005 (6)	0.0050 (3)	0.0014 (9)
C(5M)	−0.2501 (5)	0.1554 (8)	−0.6172 (6)	0.0041 (3)	0.0087 (8)	0.0037 (4)	0.0016 (8)	0.0033 (5)	0.0040 (9)
C(6)	−0.0619 (3)	−0.2285 (6)	−0.0467 (5)	0.0022 (2)	0.0036 (5)	0.0041 (3)	−0.0006 (5)	0.0032 (3)	−0.0005 (7)
C(61)	−0.0851 (3)	−0.3310 (6)	−0.0669 (5)	0.0018 (2)	0.0051 (5)	0.0042 (3)	0.0005 (5)	0.0030 (3)	0.0017 (7)
C(62)	−0.1217 (4)	−0.3651 (6)	−0.0426 (6)	0.0028 (2)	0.0050 (6)	0.0063 (4)	0.0003 (6)	0.0054 (4)	−0.0008 (8)
C(63)	−0.1412 (4)	−0.4629 (7)	−0.0586 (6)	0.0029 (2)	0.0053 (6)	0.0068 (4)	−0.0009 (6)	0.0050 (4)	0.0024 (8)
C(64)	−0.1239 (4)	−0.5244 (6)	−0.0992 (5)	0.0030 (2)	0.0052 (6)	0.0040 (3)	0.0006 (6)	0.0032 (4)	−0.0006 (7)
C(65)	−0.0877 (4)	−0.4891 (7)	−0.1251 (6)	0.0042 (2)	0.0051 (6)	0.0078 (4)	0.0018 (6)	0.0077 (4)	0.0005 (9)
C(66)	−0.0685 (3)	−0.3932 (7)	−0.1087 (5)	0.0029 (2)	0.0057 (6)	0.0082 (4)	0.0008 (5)	0.0075 (3)	−0.0012 (6)
C(6M)	−0.1462 (5)	−0.6309 (7)	−0.1173 (7)	0.0058 (3)	0.0031 (5)	0.0090 (6)	−0.0025 (7)	0.0075 (6)	−0.0017 (10)
C(71)	0.1599 (4)	−0.1198 (7)	0.0479 (8)	0.0027 (2)	0.0050 (6)	0.0177 (7)	0.0013 (6)	0.0100 (5)	0.0042 (12)
C(72)	0.1844 (4)	−0.1405 (9)	0.0035 (7)	0.0024 (2)	0.0135 (10)	0.0070 (5)	−0.0033 (8)	0.0023 (5)	0.0057 (12)
C(73)	0.2469 (5)	−0.1369 (10)	0.0477 (7)	0.0059 (2)	0.0146 (12)	0.0133 (6)	−0.0004 (10)	0.0148 (4)	0.0001 (14)
C(74)	0.2833 (4)	−0.1130 (8)	0.1384 (7)	0.0023 (2)	0.0100 (8)	0.0106 (6)	0.0027 (7)	0.0048 (5)	0.0072 (13)
C(75)	0.2553 (5)	−0.0971 (11)	0.1781 (8)	0.0044 (3)	0.0176 (13)	0.0079 (7)	−0.0065 (11)	0.0042 (7)	−0.0066 (17)
C(76)	0.1962 (5)	−0.1024 (12)	0.1351 (8)	0.0066 (3)	0.0234 (14)	0.0182 (6)	−0.0110 (11)	0.0171 (5)	−0.0283 (15)
C(81)	0.0250 (6)	0.3114 (9)	0.2935 (8)	0.0075 (3)	0.0102 (9)	0.0192 (7)	0.0039 (10)	0.0197 (5)	0.0051 (15)
C(82)	0.0497 (5)	0.3523 (12)	0.3333 (8)	0.0053 (4)	0.0166 (14)	0.0094 (7)	−0.0005 (12)	0.0072 (7)	0.0007 (18)
C(83)	0.0276 (6)	0.4780 (8)	0.2952 (8)	0.0098 (3)	0.0100 (9)	0.0161 (7)	−0.0089 (11)	0.0200 (5)	−0.0130 (13)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$. [b] Estimated standard deviations are given in parentheses.

Table III. Molecular Bond Lengths (Å) and Angles (Deg) in Mo(N₂Ph)₂(TTP)·C₆H₅NHNH₂[a]

Bond Lengths

Mo–N(1)	2.060 (5)	N(2)–C(21)	1.379 (8)	C(6)–C(11)	1.386 (8)
Mo–N(2)	2.081 (5)	C(21)–C(22)	1.422 (9)	C*(6)–C(24)	1.409 (9)[b]
Mo–N(5)	2.060 (5)	C(22)–C(23)	1.333 (9)	C(6)–C(61)	1.508 (9)
		C(23)–C(24)	1.456 (8)	C(61)–C(62)	1.362 (9)
N(5)–N(6)	1.133 (9)	C(24)–N(2)	1.367 (7)	C(62)–C(63)	1.420 (9)
N(6)–C(71)	1.448 (12)	C(5)–C(14)	1.409 (9)	C(63)–C(64)	1.362 (10)
C(71)–C(72)	1.318 (14)	C(5)–C(21)	1.385 (8)	C(64)–C(65)	1.378 (10)
C(72)–C(73)	1.384 (14)	C(5)–C(51)	1.510 (8)	C(65)–C(66)	1.393 (10)
C(73)–C(74)	1.376 (15)	C(51)–C(52)	1.372 (9)	C(66)–C(61)	1.369 (9)
C(74)–C(75)	1.311 (15)	C(52)–C(53)	1.393 (10)	C(64)–C(6M)	1.553 (9)
C(75)–C(76)	1.307 (16)	C(53)–C(54)	1.360 (10)		
C(76)–C(71)	1.307 (16)	C(54)–C(55)	1.350 (10)	C(81)–C(82)	1.288 (16)
N(1)–C(11)	1.382 (8)	C(55)–C(56)	1.383 (10)	C(82)–C(83)	1.328 (16)
C(11)–C(12)	1.437 (9)	C(56)–C(51)	1.395 (9)	C(83)–C*(83)	1.441 (29)
C(12)–C(13)	1.354 (9)	C(54)–C(5M)	1.554 (9)	C(81)–C*(81)	1.356 (27)
C(13)–C(14)	1.442 (9)			C(81)–N(7)	1.373 (18)
C(14)–N(1)	1.388 (8)			N(7)–N(8)	1.570 (22)

Bond Angles

N(1)–Mo–N(2)	89.46 (19)	Mo–N(2)–C(21)	126.55 (43)	C*(24)–C(6)–C(11)	126.08 (59)
N(1)–Mo–N(5)	87.51 (22)	Mo–N(2)–C(24)	125.25 (43)	C*(24)–C(6)–C(61)	116.08 (58)
N(2)–Mo–N(5)	91.32 (22)	N(2)–C(21)–C(22)	108.66 (57)	C(11)–C(6)–C(61)	117.83 (58)
		C(21)–C(22)–C(23)	108.16 (60)	C(6)–C(61)–C(62)	121.49 (66)
Mo–N(5)–N(6)	149.10 (93)	C(22)–C(23)–C(24)	107.73 (58)	C(61)–C(62)–C(63)	120.99 (71)
N(5)–N(6)–C(71)	128.62 (92)	C(23)–C(24)–N(2)	107.61 (58)	C(62)–C(63)–C(64)	120.36 (74)
N(6)–C(71)–C(76)	127.62 (1.63)	C(24)–N(2)–C(21)	107.85 (52)	C(63)–C(64)–C(65)	118.40 (70)
N(6)–C(71)–C(72)	114.12 (1.50)	N(2)–C(21)–C(5)	125.66 (59)	C(64)–C(65)–C(66)	120.78 (72)
C(71)–C(72)–C(73)	120.06 (1.12)	C(5)–C(21)–C(22)	125.53 (63)	C(65)–C(66)–C(61)	121.34 (73)
C(72)–C(73)–C(74)	119.74 (1.06)	N(2)–C(24)–C*(6)	125.99 (59)	C(66)–C(61)–C(62)	118.11 (66)
C(73)–C(74)–C(75)	116.11 (1.10)	C*(6)–C(24)–C(23)	126.36 (6)	C(6M)–C(64)–C(63)	119.75 (81)
C(74)–C(75)–C(76)	122.94 (1.24)	C(14)–C(5)–C(21)	126.31 (60)	C(6M)–C(64)–C(65)	121.83 (76)
C(75)–C(76)–C(71)	122.69 (1.30)	C(14)–C(5)–C(51)	116.74 (60)		
C(76)–C(71)–C(72)	118.25 (1.14)	C(21)–C(5)–C(51)	116.93 (57)	C(81)–C(82)–C(83)	123.69 (1.45)
		C(5)–C(51)–C(52)	121.36 (63)	C(82)–C(83)–C*(83)	116.60 (91)
Mo–N(1)–C(11)	125.10 (42)	C(5)–C(51)–C(56)	120.91 (63)	C(82)–C(81)–C*(81)	119.61 (91)
Mo–N(1)–C(14)	126.45 (44)	C(51)–C(52)–C(53)	119.89 (67)	C*(81)–C(81)–N(7)	104.92 (1.18)
N(1)–C(11)–C(12)	107.33 (58)	C(52)–C(53)–C(54)	122.21 (70)	C(81)–N(7)–N(8)	123.90 (1.69)
C(11)–C(12)–C(13)	108.99 (61)	C(53)–C(54)–C(55)	117.92 (70)		
C(12)–C(13)–C(14)	107.16 (61)	C(54)–C(55)–C(56)	121.81 (72)		
C(13)–C(14)–N(1)	108.04 (58)	C(55)–C(56)–C(51)	120.44 (67)		
C(14)–N(1)–C(11)	108.43 (53)	C(56)–C(51)–C(52)	117.73 (62)		
N(1)–C(11)–C(6)	126.73 (59)	C(5M)–C(54)–C(53)	119.76 (72)		
C(6)–C(11)–C(12)	125.92 (62)	C(5M)–C(54)–C(55)	122.32 (75)		
N(1)–C(14)–C(5)	125.53 (62)				
C(5)–C(14)–C(13)	126.42 (63)				

[a] Phenylhydrazine solvate atoms are labeled C(81), C(82), C(83), N(7), and N(8).   [b] C*(*i*) atom is centrosymmetric of C(*i*) atom.

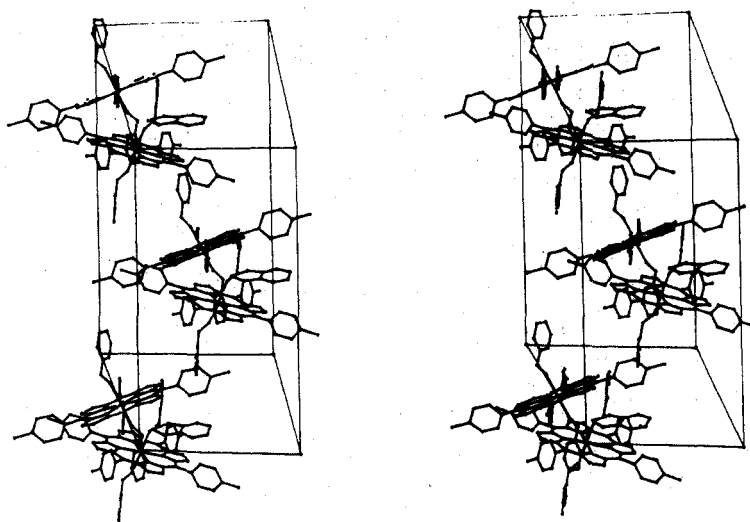**Figure 3.** Stereoscopic view of the crystal packing of Mo(N₂Ph)₂(TTP), C₆H₅NHNH₂ looking down the *z* axis. The drawing shows the two directions in which the disordered phenylhydrazine molecule was resolved.

Table IV. Least-Squares Planes for $Mo(N_2Ph)_2(TTP)$

Planes and Deviations (A)

(4N): N(1), N(2), N*(1), N*(2) (Real Plane)

(COR): N(1), C(11)–C(14), N(2), C(21)–C(24), N*(1),
C*(11)–C*(14), N*(2), C*(21)–C*(24), C(5), C(6), C*(5), C*(6)

N(1)	−0.012 (7)	N(2)	0.080 (8)
C(11)	0.015 (10)	C(21)	0.066 (10)
C(12)	−0.026 (11)	C(22)	−0.012 (10)
C(13)	−0.038 (11)	C(23)	−0.058 (11)
C(14)	−0.014 (10)	C(24)	0.007 (9)
C(5)	0.033 (9)	N(5)	2.054 (8)^a
C(6)	0.048 (10)	N(6)	2.989 (15)^a
Mo	0.000 (0)^a		

(N1): N(1), C(11), C(12), C(13), C(14)

N(1)	−0.013 (7)	C(13)	−0.002 (11)
C(11)	0.011 (10)	C(14)	0.009 (10)
C(12)	−0.006 (11)		

(N2): N(2), C(21), C(22), C(23), C(24)

N(2)	0.000 (8)	C(23)	−0.003 (11)
C(21)	−0.002 (10)	C(24)	0.002 (9)
C(22)	0.003 (10)		

(Ph5): C(51)–C(56)

C(51)	−0.006 (8)	C(55)	−0.002 (10)
C(52)	0.005 (9)	C(56)	0.004 (10)
C(53)	−0.003 (10)	C(5M)	0.034 (11)
C(54)	0.002 (9)	C(5)	−0.025 (8)^a

(Ph6): C(61)–C(66)

C(61)	−0.007 (8)	C(65)	0.005 (9)
C(62)	0.005 (9)	C(66)	0.002 (8)
C(63)	0.001 (9)	C(6M)	0.006 (11)
C(64)	−0.006 (8)	C(6)	−0.062 (7)^a

(MoN₂): Mo, N(5), N(6)

C(71)	−1.082 (11)^a	N*(2)	0.078 (6)^a

(N₂C): N(5), N(6), C(71)

Mo	−1.012 (0)^a

(Ph7): C(71), C(72), C(73), C(74), C(75), C(76)

C(71)	0.027 (10)	C(75)	0.000 (16)
C(72)	−0.011 (12)	C(76)	−0.022 (16)
C(73)	−0.009 (14)	N(6)	0.100 (11)^a
C(74)	0.015 (12)		

Equations^b

plane	A	B	C	D
(4N)	0.9220	−0.3651	−0.1288	0.0000
(COR)	0.9323	−0.3312	−0.1452	0.0001
(N1)	0.9305	−0.3280	−0.1628	0.0291
(N2)	0.9500	−0.2738	−0.1501	0.1892
(Ph5)	0.0290	−0.9711	−0.2368	0.0142
(Ph6)	−0.3687	0.2559	−0.8936	0.3011
(MoN2)	−0.3548	−0.4942	−0.7937	0.0000
(N2C)	0.5409	0.2892	−0.7898	1.0117
(Ph7)	0.0828	0.9705	−0.2263	−1.4827

Angles (Deg) between the Planes

(4N)–(COR)	2.2	(COR)–(Ph5)	67.5
(4N)–(N1)	2.9	(COR)–(Ph6)	−72.6
(4N)–(N2)	5.6	(4N)–(MoN₂)	−87.5
(N1)–(N2)	3.4	(N₂Ph)–(Ph7)	59.7

^{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^*.

The corresponding weighted factor R_w was 0.098. A p value of 0.06 was employed in the weighting scheme, and the standard deviation of a unit weight observation was 1.96. A listing of the observed and computed structure factor amplitudes is available.[10] The final positional and thermal parameters of the nonhydrogen atoms are given in Table II.

(10) Supplementary material.

Description of the Structure and Discussion.

The unit cell contains four molecules of $Mo(N_2C_6H_5)_2(TTP)$ and four phenylhydrazine solvate molecules. The molybdenum atom lies on an inversion center, implying a C_i symmetry for the whole molecule and a trans configuration for the two diazo ligands. Consequently, the molybdenum atom and the four porphyrinato nitrogen atoms are rigorously coplanar. A view of the $Mo(N_2C_6H_5)_2(TTP)$ molecule with the numbering scheme is shown in Figure 1. Bond distances and angles are presented in Table III. Figure 2 shows the atom displacements of the porphyrinato skeleton with respect to the (4N) plane. The porphyrin is not planar. Whereas two opposite pyrroles are approximately in the (4N) plane, the two others are slightly bent centrosymmetrically, one upward and the other downward. Mean planes were determined by least-squares methods (Table IV). The Mo–N(1) and Mo–N(2) bond lengths are not significantly different, 2.081 (5) and 2.060 (5) Å, and compare well with those found in other planar molybdenum–porphyrin derivatives: 2.074 (6) and 2.096 (4) Å for Mo-Cl₂(TTP)[9] and $Mo(O_2)_2(TTP)$,[11] respectively.

The bond parameters for the porphinato core are in good agreement with those reported for several metalloporphyrins.[12] With Cα and Cβ to denote the respective α- and β-carbon atoms of a pyrrole ring, Cm for methine carbon, and Cp for a phenyl carbon bonded to the core, the porphine skeleton is characterized by the averaged bond lengths N–Cα = 1.379 (4) Å, Cα–Cβ = 1.425 (5) Å, Cβ–Cβ = 1.343 (7) Å, Cα–Cm = 1.397 (5) Å, and Cm–Cp = 1.509 (6) Å. The averaged bond angles are Cα–N–Cα = 108.1 (4)°, N–Cα–Cβ = 107.9 (3)°, N–Cα–Cm = 126.0 (3)°, Cα–Cβ–Cβ = 108.0 (3)°, Cα–Cm–Cα = 126.2 (4), and Cα–Cm–Cp = 116.6 (3)°. The average value of the 12 individually determined C–C bond distances in the peripheral tolyl rings is 1.378 (3) Å. As currently observed, the tolyl groups are tilted with respect to the plane of the porphinato core; the angles of tilt are 67.5 and 72.6°.

The coordination polyhedron of molybdenum has a symmetry very close to O_h. Indeed, the aryldiazo ligands are bonded nearly perpendicularly to the porphinato core (N-(1)–Mo–N(5) = 87.51 (22)° and N(2)–Mo–N(5) = 91.32 (22)°) and the Mo–N(N₂Ph) bond distance of 2.060 (5) Å is equal to the Mo–N(pyrrole) bond distances. The two aryldiazo ligands present a "half doubly bent" geometry as reflected in the angles Mo–N(5)–N(6) = 149.1 (9)° and N(5)–N(6)–C(71) = 128.6 (9)°. To our knowledge, it is the second example of such a geometry, the other one being $[IrCl(N_2Ph)(PMePh_2)_3]PF_6$.[13] All nonbonded contacts between N(6) and the porphinato core are larger than 3.6 Å and could permit the Mo–N(5)–N(6) angle to approach the value of 120°. This intermediate geometry is well-known for nitrosyl complexes.[14] The Mo–N–N–Ph linkages eclipse the Mo–N(2) bonds as evidenced by the mean-planes calculation. The same eclipsed conformation has been previously observed for Mo-$(NO_2(TTP)$,[8] $Mo(PhC≡CPh)(TTP)$[15] and $Mo(O_2)_2(TTP)$.[11] Table V compares the observed bond angles and lengths in some aryldiazo compounds. Relatively few (aryldiazo)molybdenum complexes are known and all are singly bent species. In $Mo(N_2Ph)_2(TTP)$ the metal–nitrogen bond distance (2.060 (5) Å) is significantly longer and the N–N distance (1.133 (9) Å) is shorter than in other (aryldiazo)molybdenum com-

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(14) J. H. Enemark and R. D. Feltham, *Coord, Chem. Rev.*, **13**, 339 (1974).

(15) R. Weiss and co-workers, unpublished result.

Table V. Dimensions of Some Aryldiazo Complexes from X-ray Diffraction Studies

compd	M-N, Å	N-N, Å	N-C, Å	M-N-N, deg	N-N-C, deg	ref
Singly Bent						
Mo(N$_2$Ph)(dtc)$_3$	1.781 (4)	1.233 (6)	1.417 (7)	171.5 (4)	120.5 (5)	4b
[HB(pz)$_3$]Mo(CO)$_2$(N$_2$Ph)	1.825 (4)	1.211 (6)	1.432 (7)	174.2 (1)	121.1 (2)	3d
[IrCl(N$_2$Ph)(PPh$_3$)$_2$]$^+$	1.794	1.159	1.45	176.1	126	3a
Ru(*p*-N$_2$C$_6$H$_4$CH$_3$)Cl$_3$(PPh$_3$)$_2$	1.796 (9)	1.144 (10)	1.40	171.2 (9)	135.9 (11)	3e
Re(N$_2$Ph)Cl$_2$(PMe$_2$Ph)$_3$	1.80 (1)	1.23 (1)		172	118	4a
Doubly Bent						
[Rh(N$_2$Ph)Cl(PPP)]$^{+a}$	1.961 (7)	1.172 (9)	1.445 (11)	125.1 (6)	118.9 (8)	3f
PtCl(*p*-N$_2$C$_6$H$_4$F)(PEt$_3$)$_2$	1.975 (28)	1.17 (3)	1.49 (3)	118 (2)	118 (2)	3h
IrCl$_2$(*o*-N$_2$C$_6$H$_4$NO$_2$)(CO)(PPh$_3$)$_2$	2.05 (4)	1.19 (4)	1.47 (5)	115 (3)	115 (3)	3g
"Half Doubly Bent"						
[IrCl(N$_2$Ph)(PMePh$_2$)$_3$][PF$_6$]	1.835 (8)	1.241 (11)	1.421 (11)	1.55.2 (7)	118.8 (8)	13
Mo(N$_2$Ph)$_2$(TTP)	2.060 (5)	1.133 (9)	1.448 (12)	149.1 (9)	128.6 (9)	this work

^{a} PPP = PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$.

plexes suggesting considerably less π interaction between the metal and adjacent nitrogen of the N$_2$Ph ligand.

Usually, the M-N-N-Ph linkage is planar.[3,4] It is not the case in Mo(N$_2$Ph)$_2$(TTP) as reflected by the torsion angles (MoN$_2$,N$_2$C) = 73° and (N$_2$C,Ph$_7$) = 59.7°. This particular geometry seems to result from crystal packing. As shown in Figure 3, the phenyl group of the diazo ligand lies in a parallel and staggered position with respect to a tolyl group of a neighboring molecule. The distance between the two aromatic rings is 3.6 Å.

In addition the N(6)-N(7) distance of 2.928 Å reveals a weak hydrogen bond between the nitrogen atom N(6) of the diazo ligand and the phenylhydrazine of crystallization. As the NH group of the solvate molecule involved in this hydrogen bond with N(6) is disordered (occupancy factor of $^1/_2$), this hydrogen bond induces a slight disorder to N(6). Thus, a large thermal motion due to disorder affects N(6), and consequently the N(5)-N(6) bond length of 1.133 (9) Å is slightly too short. On the other hand, the thermal motion of N(5) is small so that the Mo-N(5) bond distance of 2.060 (5) Å is not affected by the slight disorder of N(6).

If one regards the singly bent aryldiazo as N$_2$Ph$^+$ and the doubly bent ligand as N$_2$Ph$^-$, the formal oxidation state of Mo

is correspondingly either Mo(0) or Mo(IV). In the nitrosyl derivative Mo(NO)$_2$(TTP), the two nitrosyl groups are in cis position with respect to the porphyrin ligand, and in view of the Mo-N(NO) distances (1.70 (1) Å), it may be described as a Mo(0) complex, Mo^0(NO$^+$)$_2$(TTP), despite the nonlinearity of the Mo-N-O linkage. Ignoring possible steric effects, the complexes Mo(N$_2$Ph)$_2$(TTP) and Mo(NO)$_2$(TTP) should have the same geometry if N$_2$Ph$^+$ were present, since N$_2$Ph$^+$ and NO$^+$ are formally isoelectronic. The only example of six-coordinate molybdenum(IV)–porphyrin complexes is MoCl$_2$(TTP) which exhibits two chlorines in trans configuration. Thus, considering the geometry and the Mo-N(N$_2$Ph) bond length, the present aryldiazo complex is formally best described as Mo^{IV}(N$_2$Ph)$_2$(TTP).

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Calculation of Electron-Transfer Rate Constants from the Properties of Charge-Transfer Absorption Bands. The PQ^{2+},Fe(CN)$_6^{4-}$ System

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The properties of the outer-sphere optical charge-transfer (CT) band in the ion pair Fe(CN)$_6^{4-}$,PQ^{2+} (where PQ^{2+} = 1,1′-Me$_2$-4,4′-bpy^{2+}) are used to calculate the rate constant for intermolecular electron transfer within the ion pair, Fe(CN)$_6^{4-}$,PQ^{2+} $\rightleftharpoons$ Fe(CN)$_6^{3-}$,PQ$^+$, and from that value and an appropriate thermochemical cycle, a rate constant for the overall reaction, PQ^{2+} + Fe(CN)$_6^{4-}$ $\rightarrow$ PQ$^+$ + Fe(CN)$_6^{3-}$, can be calculated (k_{12} = (0.2-3) × 10^{-4} M^{-1} s^{-1}, I = 0.10 M, 23 °C, in water). The calculated value compares well with a value estimated with the use of self-exchange rate constants for the PQ$^{2+/+}$ and Fe(CN)$_6^{3-/4-}$ couples and the Marcus cross-reaction equation (k_{12} = 10^{-3} M^{-1} s^{-1}). The results obtained suggest that for a variety of CT-type transitions it may be possible to obtain detailed information about the innate electron-transfer characteristics of the redox sites involved from a straightforward analysis of the absorption band.

The observation of optical electron transfer between electronically weakly coupled redox sites provides, in principle, a means for exploring in detail the relationships between

spectral transition energies, thermodynamics, and electron-transfer processes. Especially well documented are the low-energy transitions which appear in mixed-valence dimers or