Axial Ligand Orientation in Crystalline Modifications of Bis(2,6-lutidine-*N*-oxide)-(tetraphenylporphinato)manganese(III) Perchlorate

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(Received January 23, 1987)

Abstract

An X-ray crystallographic structure determination of a second crystalline modification of the reactive metalloporphyrin bis(2,6-lutidine-*N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate was performed. The complex crystallized as dark green rods out of a toluene/heptane solvent system in the monoclinic space group $P2_1/c$ (#14), with $a = 20.385(13)$, $b = 12.207(4)$, $c = 24.031(25)$ Å, $\beta = 113.07(7)°$; $Z = 4$. The structure was refined to final residuals of $R = 0.0692$ and $R_w = 0.0699$. The orientations of the two 2,6-lutidine-*N*-oxide axial ligands with respect to one another as well as to the porphyrin ring are nearly identical in this structure as in the structure for the purple–red prism crystalline modification of this complex ($C2/c$) reported previously. An explanation for the orientation of the axial ligands in these two complexes based on a combination of crystal packing forces and intramolecular electronic factors is presented.

Introduction

Research activity since 1980 involving the use of synthetic metalloporphyrin complexes to model various electronic, structural or catalytic features of cytochrome P-450 and to develop new systems for the homogeneous catalytic oxygenation of hydrocarbons has been intense [1–3]. Substantial efforts on the part of a number of research groups have led to the characterization of high-valent metalloporphyrin complexes that are involved directly or indirectly in the homogeneous thermal oxygenation of alkanes or alkenes catalyzed by metalloporphyrins [4]. The tractibility coupled with the potent oxidizing capabilities of the amine-*N*-oxide/metalloporphyrin systems developed largely by Bruice and coworkers [5] prompted us to isolate and characterize the electronic and structural properties of the complex bis(2,6-lutidine-*N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate (**1**) [6]. In the course of investigating further the relationship between the electronic structure and the reactivity of **1**, we attempted a crystallographic structure determination of a second crystalline modification of this complex obtained from the solvent system of highly purified toluene and n-heptane. We report here this structure and the remarkable orientation of the axial ligands that emerges when the two structures of **1** are compared.

Experimental

Materials

The solvents and reagents as well as the metalloporphyrin precursor complexes to **1** ($Mn^{III}TPPCl$ and $Mn^{III}TPPClO_4$) were obtained as described earlier [6, 7]. Complex **1** was prepared in the present study by addition of 2.5 equivalents or 0.02 g (0.163 mmol) of 2,6-lutidine-*N*-oxide to 50 mg (0.065 mmol, 1 equivalent) of $Mn^{III}TPP(ClO_4)$ in 400 ml of toluene at 100 °C. After the solution had slowly cooled to approximately 26 °C, 80 ml of n-heptane was layered on top. Two different crystalline modifications of **1**, deep purple–red prisms and dark green rods, were again produced.

X-ray Crystallography. Collection and Reduction of Intensity Data

A dark green crystal was cut from a much longer crystal and affixed to the end of a glass fiber. The fiber was then mounted on a goniometer head of a Nicolet $P2_1$ four-circle diffractometer. Cell dimensions were obtained by least-squares refinement of 16 centered reflections ($5.95° < 2\theta < 20.13°$; λ(Mo Kα) = 0.71069 Å). The ω Wyckoff scan method was used with a variable scan rate of 7.32–14.65 deg/min (scan/background = 1). Intensity measurements of 3 standards every 197 reflections showed no evidence of significant crystal deterioration. Intensities (2θ = 3°–40°) were measured for 5717 reflections of which 3788 unique reflections displayed $F_o > 2.5\sigma(F_o)$. Crystal and data collection parameters

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0020-1693/87/$3.50

TABLE I. Crystallographic Data Parameters for Green (needle) Modification of Bis(2,6-lutidine-*N*-oxide)tetraphenylporphinatomanganese(III) Perchlorate•1Heptane

(a) Crystal Data	
Formula	$C_{65}H_{64}ClMnN_6O_6$
Formula Weight	1115.6
Space group	monoclinic $P2_1/c$ (#14)
Systematic absences	$h0l$: $l = 2n + 1$ $0k0$: $k = 2n + 1$
a (A)	20.385(13)
b (A)	12.207(4)
c (A)	24.031(25)
β (°)	113.068(67)
V (A^3)	5501.88(7.24)
Z	4
D_{calc} (g cm^{-3})	1.35
Crystal dimensions (mm)	0.2 x 0.2 x 0.5
Color	dark green
μ (calc) (cm^{-1})	3.7
(b) Data Collection	
Diffractometer	Syntex (Nicolet) $P2_1$
Radiation (monochromatic)	Mo Kα (λ = 0.71069)
R (merge), R (sigma)	0.0062, 0.0514
Total reflections measured independent	5717/3788 $F_o > 2.5\sigma F_0$
Scan method	ωWyckoff
2θ Range (°)	3–40
Scan speed (° min^{-1})	7.32–14.65
Background/scan time	1
Reflections measured	$\pm h$, $+k$, $+l$
Temperature (°C)	20
(c) Refinement	
Absorption correction	none
Maximum residual electron density (e A^{-3})	0.64 (1.45 A from Cl)
R^a	0.0692
$R_w{}^b$	0.0699
GOF^c	1.500

$^aR = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]$. ^cGOF (goodness of fit) = $[\Sigma w(|F_o| - |F_c|)^2 / n_o - n_v]^{1/2}$ where n_o is the number of observations, n_v is the number of parameters, and $w^{-1} = (\sigma^2(F) + |0.0012|F^2)$.

along with the values for the residuals after final refinement are summarized in Table I.

Structure Solution and Refinement

The computer hardware and software for data refinement and structure solution were described previously [6, 7]. The space group was uniquely determined to be monoclinic $P2_1/c$ (#14) with systematic absences hkl:$h0l$:$l = 2n + 1$, $0k0$:$k = 2n + 1$. The structure was solved using Patterson and Fourier syntheses to locate the Mn atom and other non-hydrogen atoms. Hydrogen atoms were placed in their calculated positions and were allowed to 'ride' on their parent carbon atoms [C–H = 0.96 Å; U_{iso}(H) = 1.2 U_{ij}(C)]. All nonhydrogen atoms were refined anisotropically. The final electron density difference map was featureless with the maximum positive peak 0.64 e $Å^{-3}$ at a distance of 1.45 Å from Cl of the perchlorate. Blocked-cascade least-squares refinement of 703 variables gave final agreement factors of $R = 0.0692$, $R_w = 0.0699$, and $GOF* = 1.500$ (see Table I for definitions of R, R_w and GOF). On the last cycle of the least-squares refinement, the ratio of the maximum shift to the estimated standard deviation was 0.051. Psi-scan data showed intensity changes of less than 10% therefore the data was not corrected for absorption. A weighting scheme utilizing weights of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ (where $g = 0.0012$) was implemented. Scattering factors were those used for neutral atoms [8]. The final positional and thermal parameters are given in Table II.

TABLE II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($A^2 \times 10^3$)

Atom	x	y	z	U^a
Mn	3528(1)	6525(1)	1656(1)	32(1)*
O(1b)	3478(2)	8406(4)	1610(2)	52(2)*
O(1a)	3688(2)	4688(4)	1746(2)	49(2)*
N(1)	3315(3)	6478(4)	2395(2)	32(2)*
N(2)	2502(2)	6440(4)	1150(2)	34(2)*
N(3)	3741(3)	6593(4)	913(2)	32(2)*
N(4)	4562(2)	6599(4)	2167(2)	30(2)*
C(1)	3793(3)	6223(5)	2981(3)	30(3)*
C(2)	3411(3)	6192(5)	3369(3)	42(3)*
C(3)	2730(3)	6467(5)	3040(3)	41(3)*
C(4)	2647(3)	6619(5)	2424(3)	35(3)*
C(5)	2004(3)	6752(5)	1925(3)	36(3)*
C(6)	1941(3)	6612(5)	1331(3)	38(3)*
C(7)	1274(4)	6519(6)	814(3)	48(3)*
C(8)	1427(4)	6270(6)	332(3)	52(4)*
C(9)	2190(4)	6234(5)	533(3)	40(3)*
C(10)	2552(4)	6163(5)	153(3)	35(3)*
C(11)	3271(3)	6387(5)	329(3)	35(3)*
C(12)	3639(4)	6474(6)	−66(3)	44(3)*
C(13)	4318(4)	6757(5)	276(3)	45(3)*
C(14)	4407(3)	6800(5)	890(3)	34(3)*
C(15)	5041(3)	6947(5)	1381(3)	30(3)*
C(16)	5108(3)	6839(5)	1978(3)	32(3)*
C(17)	5772(3)	6801(5)	2499(3)	41(3)*
C(18)	5632(3)	6510(5)	2974(3)	37(3)*
C(19)	4870(3)	6374(5)	2782(3)	32(3)*
C(20)	4520(3)	6131(5)	3157(3)	28(3)*
C(21)	4982(3)	5805(5)	3786(3)	30(3)*
C(22)	5002(3)	6416(6)	4281(3)	38(3)*
C(23)	5473(4)	6148(6)	4861(3)	49(3)*
C(24)	5940(3)	5278(6)	4952(3)	49(3)*
C(25)	5908(4)	4647(6)	4466(3)	45(3)*

(continued)

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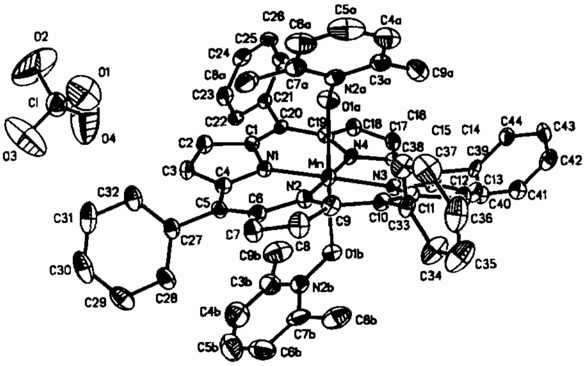
*Goodness of fit.

TABLE II. *(continued)*

Atom	x	y	z	U^a
C(26)	5424(3)	4901(6)	3885(3)	39(3)*
C(27)	1327(3)	6951(6)	2019(3)	41(3)*
C(28)	940(4)	7896(6)	1795(3)	54(4)*
C(29)	306(4)	8090(8)	1858(4)	66(4)*
C(30)	63(5)	7339(11)	2149(4)	80(5)*
C(31)	422(5)	6401(10)	2363(4)	75(5)*
C(32)	1066(4)	6196(7)	2305(3)	58(4)*
C(33)	2129(3)	5846(6)	−494(3)	41(3)*
C(34)	1965(4)	6602(7)	−944(4)	67(4)*
C(35)	1566(4)	6305(9)	−1542(4)	85(5)*
C(36)	1346(4)	5228(9)	−1671(4)	77(4)*
C(37)	1492(4)	4476(7)	−1227(4)	72(4)*
C(38)	1883(4)	4782(6)	−636(3)	52(3)*
C(39)	5717(3)	7095(6)	1278(3)	33(3)*
C(40)	6121(4)	8040(6)	1477(3)	38(3)*
C(41)	6762(4)	8167(7)	1410(3)	48(4)*
C(42)	6989(4)	7357(7)	1138(3)	55(4)*
C(43)	6593(4)	6416(7)	935(3)	54(4)*
C(44)	5952(4)	6282(6)	1002(3)	43(3)*
N(2a)	3332(3)	3918(4)	1355(3)	41(2)*
C(3a)	3594(4)	3543(6)	945(4)	53(4)*
C(4a)	3198(4)	2739(7)	539(3)	70(4)*
C(5a)	2567(5)	2338(7)	559(4)	85(5)*
C(6a)	2364(5)	2700(7)	990(5)	73(5)*
C(7a)	2742(4)	3482(6)	1391(3)	48(3)*
C(8a)	2526(4)	3881(7)	1887(4)	77(5)*
C(9a)	4273(5)	3974(7)	976(4)	88(5)*
N(2b)	3022(3)	9056(5)	1721(3)	50(3)*
C(3b)	3195(4)	9398(6)	2304(4)	67(4)*
C(4b)	2747(5)	10043(7)	2437(4)	94(5)*
C(5b)	2121(6)	10385(8)	1991(5)	111(7)*
C(6b)	1970(5)	10077(7)	1401(5)	89(5)*
C(7b)	2435(4)	9414(6)	1257(4)	63(4)*
C(8b)	2329(5)	9079(8)	634(4)	89(5)*
C(9b)	3891(5)	9064(7)	2767(4)	93(5)*
C1	1640(1)	4647(2)	3934(1)	76(1)*
O(1)	1522(4)	4163(7)	3373(3)	143(5)*
O(2)	1716(8)	3840(10)	4311(5)	262(10)*
O(3)	1075(5)	5219(10)	3892(6)	229(8)*
O(4)	2241(5)	5226(11)	4114(5)	245(8)*
C(45)	566(7)	2683(20)	−41(9)	244(13)*
C(46)	507(6)	3550(13)	531(11)	211(13)*
C(47)	221(9)	3434(23)	1291(9)	296(16)*
C(48)	233(10)	2726(20)	892(10)	397(17)*
C(49)	76(7)	1718(13)	686(8)	201(10)*
C(50)	283(7)	1673(13)	90(8)	214(10)*

[a] Starred items, equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Results and Discussion



Figl 1. ORTEP and atom numbering diagram for the green needle modification ($P2_1/c$) of **1**. Thermal ellipsoids at 30% probability level. The disordered n-heptane molecule of solvation and the hydrogen atoms have been omitted for clarity.

A combination ORTEP and atom numbering diagram of the green crystalline modification of the title complex bis(2,6-lutidine-*N*-oxide)(tetraphenylporphinato)manganese(III) perchlorate (**1**) is given in Fig. 1. Bond distances and angles for the complex (selected values given in Table III) are very similar to those seen in the purple–red prism modification of **1** ($C2/c$) reported earlier. The second structure ($P2_1/c$) shows slightly less S_4 ruffling of the porphyrin ring than that seen in the $C2/c$ structure. The maximum displacements above and below the mean 24 atom porphyrin planes in the $P2_1/c$ structure are 0.473 and –0.454 Å while those in the $C2/c$ structure are 0.463 and –0.461 Å. The displacement of the manganese atom from the mean N_4 plane is 0.024 Å in the $P2_1/c$ structure *versus* 0.0007 Å for the $C2/c$ structure. The electronic and structural features of **1** were investigated in some detail earlier [6]. The noteworthy feature in this work is the nearly identical orientation of the two oxygen donating axial ligands with respect to one another as well as the porphyrin ring in the two different crystal structures. The torsion angle defined by atoms N2b, O1b, O1a, and N2a of the two 2,6-lutidine-*N*-oxide ligands in the second structure ($P2_1/c$) is 82.7°. This angle defined by the same atoms in the first structure is 82.1°. Furthermore as is evident in Fig. 2, the orientation of the two 2,6-lutidine-*N*-oxide ligands with respect to the porphyrin ring (eclipsing the *meso* porphyrin carbons and straddling the pyrrole moieties), is very similar in the two structures. Finally, the tilt angles defined by the planes of the lutidine rings and the porphyrin ring are nearly the same. The two tilt angles in the $P2_1/c$ structure are 135.3° and 118.4°; those in the $C2/c$ structure are 135.5° and 116.8°!

The correspondence of axial ligand orientation in **1** between the two different space groups is remarkable. An examination of the intermolecular close nonbonded contacts between the atoms of the 2,6-lutidine-*N*-oxide axial ligands and the atoms of adjacent groups in the unit cells of the two structures does not indicate that the observed conformations of the axial ligands in either structure of **1** are obviously dictated by such contacts. However, an

TABLE III. Selected Bond Distances (Å) And Angles (°) in the Green Needle Modification of 1

Mn–O(1b)	2.300(5)	Mn–O(1a)	2.263(5)
Mn–N(1)	1.987(6)	Mn–N(2)	1.966(4)
Mn–N(3)	1.998(6)	Mn–N(4)	1.982(4)
O(1b)–N(2b)	1.324(9)	O(1a)–N(2a)	1.326(7)
N(1)–C(1)	1.398(7)	N(1)–C(4)	1.402(9)
N(2)–C(6)	1.390(10)	N(2)–C(9)	1.387(8)
N(3)–C(11)	1.378(7)	N(3)–C(14)	1.402(9)
N(4)–C(16)	1.389(9)	N(4)–C(19)	1.388(7)
C(1)–C(2)	1.432(11)	C(1)–C(20)	1.376(9)
C(2)–C(3)	1.342(8)	C(3)–C(4)	1.435(10)
C(4)–C(5)	1.396(8)	C(5)–C(6)	1.393(11)
C(5)–C(27)	1.504(11)	C(6)–C(7)	1.442(8)
C(7)–C(8)	1.348(12)	C(8)–C(9)	1.438(10)
C(9)–C(10)	1.384(12)	C(10)–C(11)	1.384(10)
C(10)–C(33)	1.504(8)	C(11)–C(12)	1.428(12)
C(12)–C(13)	1.350(9)	C(13)–C(14)	1.417(10)
C(14)–C(15)	1.378(7)	C(15)–C(16)	1.391(10)
C(15)–C(39)	1.504(10)	C(16)–C(17)	1.440(7)
C(17)–C(18)	1.329(11)	C(18)–C(19)	1.445(9)
C(19)–C(20)	1.385(11)	C(20)–C(21)	1.489(8)
N(2a)–C(3a)	1.370(12)	N(2a)–C(7a)	1.349(10)
C(3a)–C(4a)	1.396(10)	C(3a)–C(9a)	1.455(13)
C(4a)–C(5a)	1.395(14)	C(5a)–C(6a)	1.331(17)
C(6a)–C(7a)	1.361(11)	C(7a)–C(8a)	1.504(14)
N(2b)–C(3b)	1.370(11)	N(2b)–C(7b)	1.349(9)
C(3b)–C(4b)	1.337(15)	C(3b)–C(9b)	1.477(11)
C(4b)–C(5b)	1.371(13)	C(5b)–C(6b)	1.380(16)
C(6b)–C(7b)	1.388(14)	C(7b)–C(8b)	1.484(14)
Cl–O(1)	1.403(9)	Cl–O(2)	1.305(12)
Cl–O(3)	1.315(12)	Cl–O(4)	1.331(12)
O(1b)–Mn–O(1a)	174.7(2)	O(1b)–Mn–N(1)	92.9(2)
O(1a)–Mn–N(1)	87.7(2)	O(1b)–Mn–N(2)	90.4(2)
O(1a)–Mn–N(2)	94.9(2)	N(1)–Mn–N(2)	90.0(2)
O(1b)–Mn–N(3)	86.4(2)	O(1a)–Mn–N(3)	93.1(2)
N(1)–Mn–N(3)	179.2(2)	N(2)–Mn–N(3)	90.0(2)
O(1b)–Mn–N(4)	90.0(2)	O(1a)–Mn–N(4)	84.7(2)
N(1)–Mn–N(4)	90.0(2)	N(2)–Mn–N(4)	179.6(2)
N(3)–Mn–N(4)	90.0(2)	Mn–O(1b)–N(2b)	127.6(4)
Mn–O(1a)–N(2a)	128.1(3)	Mn–N(1)–C(1)	126.6(5)
Mn–N(1)–C(4)	126.6(4)	C(1)–N(1)–C(4)	106.6(6)
Mn–N(2)–C(6)	127.2(4)	Mn–N(2)–C(9)	127.1(5)
C(6)–N(2)–C(9)	105.7(5)	Mn–N(3)–C(11)	126.4(5)
Mn–N(3)–C(14)	126.5(4)	C(11)–N(3)–C(14)	106.9(6)
Mn–N(4)–C(16)	127.0(4)	Mn–N(4)–C(19)	125.3(5)
C(16)–N(4)–C(19)	107.6(5)	N(1)–C(1)–C(2)	108.6(5)
N(1)–C(1)–C(20)	124.7(7)	C(2)–C(1)–C(20)	126.4(5)
C(1)–C(2)–C(3)	108.1(6)	C(2)–C(3)–C(4)	108.6(7)
N(1)–C(4)–C(3)	108.0(5)	N(1)–C(4)–C(5)	125.1(7)
C(3)–C(4)–C(5)	126.4(7)	C(4)–C(5)–C(6)	123.0(7)
C(4)–C(5)–C(27)	119.8(7)	C(6)–C(5)–C(27)	116.9(5)
N(2)–C(6)–C(5)	125.6(5)	N(2)–C(6)–C(7)	109.5(6)
C(5)–C(6)–C(7)	124.7(7)	C(6)–C(7)–C(8)	107.4(7)
C(7)–C(8)–C(9)	107.6(6)	N(2)–C(9)–C(8)	109.8(7)
N(2)–C(9)–C(10)	125.2(6)	C(8)–C(9)–C(10)	124.4(6)
C(9)–C(10)–C(11)	124.0(6)	C(9)–C(10)–C(33)	117.5(6)
C(11)–C(10)–C(33)	118.5(7)	N(3)–C(11)–C(10)	125.4(7)
N(3)–C(11)–C(12)	109.1(6)	C(10)–C(11)–C(12)	125.5(5)
C(11)–C(12)–C(13)	107.2(6)	C(12)–C(13)–C(14)	109.0(7)
N(3)–C(14)–C(13)	107.7(5)	N(3)–C(14)–C(15)	126.0(6)

(continued)

TABLE III. *(continued)*

C(13)–C(14)–C(15)	126.2(7)	C(14)–C(15)–C(16)	123.4(7)
C(14)–C(15)–C(39)	119.2(6)	C(16)–C(15)–C(39)	117.0(5)
N(4)–C(16)–C(15)	126.0(5)	N(4)–C(16)–C(17)	108.0(6)
C(15)–C(16)–C(17)	125.5(7)	C(16)–C(17)–C(18)	108.2(6)
C(17)–C(18)–C(19)	108.7(5)	N(4)–C(19)–C(18)	107.5(6)
N(4)–C(19)–C(20)	127.0(5)	C(18)–C(19)–C(20)	125.4(5)
C(1)–C(20)–C(19)	123.4(5)	C(1)–C(20)–C(21)	120.7(6)
C(19)–C(20)–C(21)	115.8(5)	C(20)–C(21)–C(22)	121.4(6)
O(1a)–N(2a)–C(7a)	119.2(6)	O(1a)–N(2a)–C(3a)	119.2(6)
N(2a)–C(3a)–C(4a)	117.1(8)	C(3a)–N(2a)–C(7a)	121.6(6)
C(4a)–C(3a)–C(9a)	124.6(9)	N(2a)–C(3a)–C(9a)	118.2(7)
C(4a)–C(5a)–C(6a)	118.8(8)	C(3a)–C(4a)–C(5a)	120.7(9)
N(2a)–C(7a)–C(6a)	120.2(9)	C(5a)–C(6a)–C(7a)	121.4(9)
C(6a)–C(7a)–C(8a)	121.9(8)	N(2a)–C(7a)–C(8a)	118.0(6)
O(1b)–N(2b)–C(7b)	119.6(6)	O(1b)–N(2b)–C(3b)	117.9(6)
N(2b)–C(3b)–C(4b)	119.9(7)	C(3b)–N(2b)–C(7b)	122.3(8)
C(4b)–C(3b)–C(9b)	121.8(8)	N(2b)–C(3b)–C(9b)	118.2(8)
C(4b)–C(5b)–C(6b)	119.1(11)	C(3b)–C(4b)–C(5b)	120.4(10)
N(2b)–C(7b)–C(6b)	117.1(9)	C(5b)–C(6b)–C(7b)	121.0(8)
C(6b)–C(7b)–C(8b)	124.6(7)	N(2b)–C(7b)–C(8b)	118.3(8)

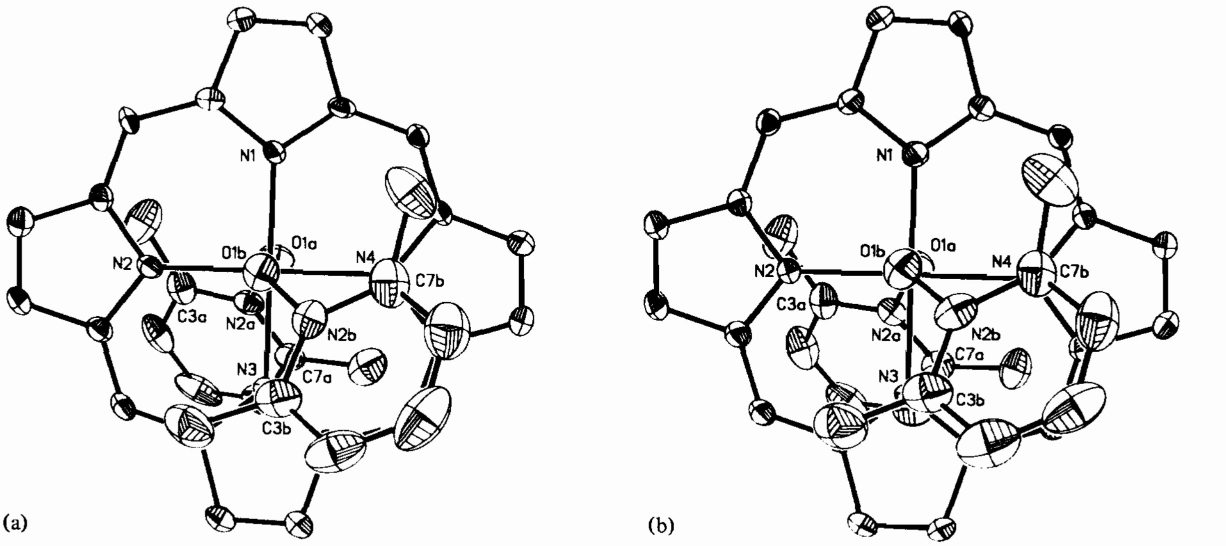


Fig. 2. Views down the axis normal to the mean 24-atom porphyrin plane for the two structures of 1. Left (a), the green needle modification ($P2_1/c$); right (b), the purple-red prism modification ($C2/c$). Phenyl groups and hydrogen atoms omitted for clarity.

examination of the molecular packing in both unit cells indicates that the striking similarity of axial ligand geometry in the two structures is dictated, at least in part, by crystal packing forces. Two of the lattice parameters 'b' and 'c', are very similar in the two crystals. Both structures are made up of similar planes and only the stacking of these planes is different. Some of the nonbonded distances that specify key distances between the (tetraphenylporphinato)manganese(III) and the perchlorate moieties in the two structures are given in Table IV. Clearly some of these key distances including the $d_{\mathrm{Mn-Mn}}$ are effectively identical, while others are not.

Although possible, it strains credibility to attribute the extreme similarity of the relative orientations of the axial ligands in the two different crystalline forms of 1 solely to crystal packing forces. Examination of the frontier orbitals of both the porphyrin ring and the 2,6-lutidine-*N*-oxide groups along with bond distance and angle data indicates the presence of

TABLE IV. Close Nonbonded Distances (A) Involving the Manganese Atoms of the Metalloporphyrins and the Chlorine Atoms of the Perchlorates in the Two Crystal Structures of 1.

Green needle modification ($P2_1/c$)		Red–purple prism modification ($C2/c$)	
Mn···Mn (2)	8.406	Mn···Mn	8.405 8.394
Mn···Cl	7.728 8.158 9.728	Mn···Cl	7.546 8.235 9.775
Cl···Cl	9.661 9.925	Cl···Cl	8.487 9.126

possible electronic donor–acceptor interactions that may contribute to the observed axial ligand orientations. Weak orbital overlap could occur between the lutidine nitrogen atom orbitals and the large lobe of the lowest unoccupied porphyrin ring $4e_g(\pi^*)$ orbital at the *meso* carbon atoms (N2b–C5 = 3.641 Å and N2a–C10 = 3.846 Å). An additional interaction probably less likely given the energies of the lutidine ring π^* orbitals, is an electron donor–acceptor interaction in the opposite direction. Specifically, donation of electron density from the large lobes at the nitrogen atoms of the high energy occupied $a_{2u}(\pi)$ and $3e_g(\pi)$ porphyrin ring orbitals to the lutidine ring π^* orbitals. Certainly one would not expect such donor–acceptor interactions to be strong. Furthermore it is clear that there is free rotation about the Mn–O and/or N–O bonds of 1 in solution on the ^{1}H NMR time scale to at least −40 °C [6]. The axial ligand–porphyrin ring interactions are likely less than 10 kcal/mol. Nevertheless such weak intramolecular interactions could be sufficient to cause the O–Mn–O angle in the two crystal structures of 1 (174.7(2)° for the $P2_1/c$ structure and 173.2(2)° for the $C2/c$ structure) to deviate from 180°. Electron donor–acceptor character in π-complexes between aromatic or other organic molecules and metalloporphyrin complexes [9, 10] as well as the electronic and steric basis of axial ligand conformations for axial aromatic nitrogen bases on metalloporphyrins [11, 12] have been addressed in both solution and solid state studies. The weak and more remote intramolecular electronic effects on metalloporphyrin axial ligand orientation presented in this work have not been noted before.

In summary, we attribute the control of axial orientation in 1 primarily to crystal packing forces and secondarily to weak intramolecular porphyrin–lutidine electronic interactions.

Acknowledgement

This research is supported by the National Science Foundation (grant no. CHE-8402994).

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