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The Crystal and Molecular Structure of Bis(methanol)-α,β,γ,δ-tetraphenylporphinatomanganese(III) Perchlorate-Methanol. A Molecular Structure Relevant to the Intermediate-spin Six Coordinate Iron(III) Porphyrin

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Bis(methanol)-α,β,γ,δ-tetraphenylporphinatomanganese(III) perchlorate crystallizes as the methanol solvate in the triclinic system, space group $P\bar{1}$, $a=16.225(8)$, $b=13.167(7)$, $c=10.793(5)$ Å, $\alpha=106.51(5)°$, $\beta=100.36(5)°$, $\gamma=101.60(5)°$, and $Z=2$. The structure was determined by the heavy-atom method and the block-diagonal least-squares refinement using a total of 9992 reflections. The final R and R_w values are 6.3 and 7.1%, respectively. Two slightly different but substantially identical coordination spheres of high-spin Mn(III) porphyrin were revealed. The long axial Mn–O(methanol) bond distance and medium-sized porphyrin core were emphasized as structural characteristics in relation to the intermediate-spin iron(III) porphyrin.

Althoug there is no support for the idea that manganese chlorophyll or porphyrin is involved in photosynthesis, the photochemistry of manganese[1,2)] and other metal porphyrins[3–5)] is interesting to explore the possibility of the solar energy conversion imitating biological systems. In a previous paper,[3)] we reported the photochemical reduction of the central metal ions of some metal-TPPS[6)] by alcohols ligating the axial positions. The coordination of weakly ligating substances, *e.g.*, water, alcohol, and DMSO, to metalloporphyrins has only recently been established by the definitive X-ray studies.[7–9,22)] Thus, this work aims, at first, to establish the explicit occupation of methanols on the axial positions of MnTPP$^+$ as a basis of our interpretation of the photochemical reaction mechanism of Mn-porphyrins in alcoholic solution.

On the other hand, the extensive studies of the spin state/stereochemistry relationship in metalloporphyrins conducted by Scheidt and co-workers have proposed two structural types of intermediate-spin iron(III) porphyrins,[10–12)] namely five coordination[10,11,13)] and six-coordination.[12)] The high-spin state of Mn(III) porphyrins has an electron configuration analogous to the intermediate-spin iron(III) porphyrins, *i.e.*, unoccupied $d_{x^2-y^2}$ and singly occupied d_{z^2}. The crystal structure of the high-spin six-coordinate MnTPP$^+$ is a proper example for supporting the assignment of structural characteristics of the six-coordinate intermediate-spin iron(III) porphyrin.

Experimental

Preparation. The starting manganese porphyrin, MnTPP(OH), which has not yet been characterized definitively, was prepared as described previously.[14)] All other chemicals and solvents were reagent grade and used without further purification.

A chloroform solution of MnTPP(OH) (200 mg/100 ml) was shaken with an aqueous $HClO_4$ solution (*ca.* 10%) in a separatory funnel. The chloroform layer was separated and evaporated to dryness under reduced pressure. The resulting solid was extracted with methanol. Single crystals of MnTPP$(CH_3OH)_2ClO_4\cdot CH_3OH$ were obtained by slow evaporation of solvent from the solution (yield: 100 mg as crystals). The crystals appear to lose easily the methanol molecule of solvation; hence freshly prepared crystals were sealed into thin-walled glass capillaries.

The infrared spectrum of the crystalline material was obtained as a KBr pellet on a JASCO IRA-2 spectrometer. The intence and broad absorption centered at 1090 cm^{-1} and the strong, sharp band at 620 cm^{-1} were consistent with the assignment of free perchlorate ion.[15)]

Found: C, 65.69; H, 3.88; N, 6.72%. Calcd for $MnC_{47}H_{40}N_4ClO_7$: C, 65.40; H, 4.68; N, 6.50%. The low value found for hydrogen may be due to loss of methanol. UV (CH_3OH) λ_{max} (log ε): 597 (3.66), 564 (3.80), 514 (3.54), 467 (4.74), 439 (4.14), 399 (4.50), and 378 nm (4.50).

Magnetic Measurement in Solution. The Evans NMR method[16)] was applied to measure the magnetic susceptibility of this Mn(III) porphyrin, using a coaxial NMR double tube (4 mm o.d.) purchased from Nippon Seimitsukagaku Co., Ltd. TMS in $CDCl_3$ (*ca.* 2 vol%) was used as the tracer signals in the reference and sample in the tube, since TMS would not coordinate to the metalloporphyrin. A 0.166 ppm splitting of the TMS ptotons in 7.8 mmol dm^{-3} MnTPP$^+$ solution from the reference was observed in the spectrum recorded on a JEOL FX-100 spectrometer operating at 99.5 MHz radiowave frequency and at 20 °C. The magnetic moment was calculated with diamagnetic corrections according to the reported equation.[16)] The μ_{eff} was 5.3 μ_B.

Crystal Structure Determination. A crystal of MnTPP$(CH_3OH)_2ClO_4\cdot CH_3OH$ with approximate dimensions of $0.5\times 0.7\times 0.9$ mm was mounted in a thin-walled capillary. Lattice constants were determined by the angular settings for 18 carefully centered reflections on a Philips PW-1100 four-circle X-ray diffractometer. Crystallographic data at 20 ± 1 °C ($\lambda=0.71069$ Å): triclinic, $a=16.225(8)$, $b=13.167(7)$, $c=10.793(5)$ Å, $\alpha=106.51(5)°$, $\beta=100.36(5)°$, $\gamma=101.60(5)°$, the unit cell volume $(U)=2095.6$ Å^3, $Z=2$, the calculated density $(D_x)=1.368$ g/cm^3, and the experimentally determined density $(D_m)=1.373$ g/cm^3.

Intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation and θ-2θ scanning. All independent reflections for which $(\sin\theta)/\lambda<0.704$ Å^{-1} were measured. A total of 9992 reflections (81% of the theoretical number possible) having F_o greater than $2\sigma(F_o)$ were used in the solution and refinement of structure. No absorption or extinction correction was made. Data collection and reduction were carried out at the Unversity of Tokyo.

A Patterson map revealed that the manganese atoms are

TABLE 1. FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR MnTPP $(CH_3OH)_2ClO_4CH_3OH$[a, c]

Atom	x	y	z	$B_{eq}^{b)}$/Å^2	Atom	x	y	z	$B_{eq}^{b)}$/Å^2
Mn_1	0.0	0.0	0.0	2.6	C_{a8}	0.51354(14)	0.74458(17)	0.0599(2)	3.2
N_1	0.10089(11)	0.11137(14)	−0.01103(17)	2.9	C_{b5}	0.31083(15)	0.26378(19)	−0.3361(2)	3.9
N_2	0.07536(11)	−0.01895(15)	0.15607(17)	3.1	C_{b6}	0.29217(14)	0.35580(19)	−0.3499(2)	3.5
C_{a1}	0.10233(14)	0.16325(18)	−0.1058(2)	3.3	C_{b7}	0.41506(16)	0.75826(19)	−0.1049(2)	3.7
C_{a2}	0.18504(13)	0.14401(18)	0.0674(2)	3.1	C_{b8}	0.47534(17)	0.81815(18)	0.0094(3)	4.0
C_{a3}	0.16356(13)	0.03050(19)	0.2105(2)	3.3	C_{m3}	0.35628(13)	0.55717(17)	−0.2310(2)	3.1
C_{a4}	0.05089(14)	−0.08458(19)	0.2301(2)	3.4	C_{m4}	0.42146(14)	0.22398(17)	−0.1766(2)	3.0
C_{b1}	0.18776(15)	0.2305(2)	−0.0835(3)	4.1	C_{13}	0.29271(14)	0.57882(17)	−0.3330(2)	3.2
C_{b2}	0.23885(14)	0.2186(2)	0.0224(2)	3.9	C_{14}	0.22190(16)	0.6141(2)	−0.3027(2)	4.0
C_{b3}	0.19362(15)	−0.0050(2)	0.3198(3)	4.3	C_{15}	0.16184(17)	0.6289(2)	−0.4005(3)	4.7
C_{b4}	0.12497(15)	−0.0748(2)	0.3325(3)	4.3	C_{16}	0.17323(17)	0.6109(2)	−0.5279(3)	4.7
C_{m1}	0.03202(14)	0.15089(19)	−0.2094(2)	3.4	C_{17}	0.24271(19)	0.5757(3)	−0.5582(3)	5.3
C_{m2}	0.21461(13)	0.10578(19)	0.1701(2)	3.3	C_{18}	0.30299(16)	0.5599(2)	−0.4610(3)	4.4
C_1	0.04592(14)	0.2100(2)	−0.3071(2)	3.8	C_{19}	0.39020(14)	0.10479(17)	−0.2637(2)	3.3
C_2	0.0614(2)	0.1570(3)	−0.4258(3)	5.2	C_{20}	0.41239(18)	0.0737(2)	−0.3846(3)	4.3
C_3	0.0698(2)	0.2086(3)	−0.5207(3)	6.5	C_{21}	0.38048(19)	−0.0342(2)	−0.4711(3)	5.0
C_4	0.06461(18)	0.3129(3)	−0.4946(3)	6.9	C_{22}	0.32638(18)	−0.1095(2)	−0.4368(3)	5.2
C_5	0.0510(2)	0.3687(3)	−0.3753(4)	7.5	C_{23}	0.30589(18)	−0.0808(2)	−0.3178(4)	5.7
C_6	0.0409(2)	0.3159(3)	−0.2820(3)	6.1	C_{24}	0.33817(18)	0.0270(2)	−0.2283(3)	4.8
C_7	0.30995(14)	0.1468(2)	0.2408(2)	3.6	O_1	0.03894(12)	−0.13380(15)	−0.13905(18)	4.7
C_8	0.36433(16)	0.0783(2)	0.2173(3)	4.7	C_{25}	0.1158(2)	−0.1178(3)	−0.1854(4)	8.2
C_9	0.45196(17)	0.1158(3)	0.2844(3)	5.7	O_2	0.39428(11)	0.49369(16)	0.11212(17)	4.7
C_{10}	0.48426(16)	0.2203(3)	0.3739(3)	5.8	C_{26}	0.4099(3)	0.5113(4)	0.2488(4)	8.7
C_{11}	0.43135(19)	0.2884(3)	0.3978(3)	5.6	O_3	0.0316(3)	−0.3186(3)	−0.0896(6)	18.1
C_{12}	0.34371(17)	0.2515(2)	0.3311(3)	4.8	C_{27}	−0.0420(8)	−0.4021(5)	−0.1214(7)	21.4
Mn_2	0.5	0.5	0	2.5	Cl	0.23990(9)	0.68149(11)	0.11689(11)	10.3
N_3	0.40851(11)	0.40986(14)	−0.16794(16)	2.8	O_4	0.2584(3)	0.5857(4)	0.0459(4)	14.5
N_4	0.47576(11)	0.63783(14)	−0.02561(17)	2.8	O_5	0.2343(3)	0.7510(4)	0.0415(4)	16.6
C_{a5}	0.38351(13)	0.29652(17)	−0.2233(2)	2.9	O_6	0.1680(3)	0.6638(4)	0.1668(6)	19.1
C_{a6}	0.35356(13)	0.44739(17)	−0.2468(2)	3.0	O_7	0.3105(4)	0.7325(5)	0.2312(5)	19.4
C_{a7}	0.41363(14)	0.64541(17)	−0.1263(2)	3.2					

a) The estimated standard deviations of the least significant digits are given in parentheses. b) Parameters as calculated from $B_{eq}=4/3(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2+1/2(\beta_{12}\ ab\ \cos\gamma+\beta_{13}\ ac\cos\beta+\beta_{23}\ bc\cos\alpha))$, where β_{ij} are dimensionless thermal values employed during computation as $\exp(-\sum_{j\geq i}\beta_{ji}h_ih_j)$. c) The atoms labeled Mn_2 to C_{24} and O_2 to C_{26} in this Table belong to the second molecule shown in Fig. 4.[30]

TABLE 2. SELECTED INTERATOMIC DISTANCES FOR MnTPP$(CH_3OH)_2$ ClO_4CH_3OH[a]

Bond distance	l/Å		l/Å	Bond distance	l/Å		l/Å
Mn_1–N_1	2.011(2)	C_{a7}–C_{b7}	1.434(4)	C_1–C_2	1.369(4)	C_{18}–C_{13}	1.378(4)
Mn_1–N_2	1.998(2)	C_{a8}–C_{b8}	1.425(4)	C_2–C_3	1.386(5)	C_{19}–C_{20}	1.386(4)
Mn_2–N_3	2.004(2)	C_{a1}–C_{m1}	1.392(3)	C_3–C_4	1.347(6)	C_{20}–C_{21}	1.397(4)
Mn_2–N_4	2.012(2)	C_{a2}–C_{m2}	1.386(3)	C_4–C_5	1.372(6)	C_{21}–C_{22}	1.363(5)
N_1–C_{a1}	1.376(3)	C_{a3}–C_{m2}	1.377(4)	C_5–C_6	1.386(6)	C_{22}–C_{23}	1.353(5)
N_1–C_{a2}	1.382(3)	C_{a4}–C'_{m1}	1.390(3)	C_6–C_1	1.367(4)	C_{23}–C_{24}	1.407(5)
N_2–C_{a3}	1.388(3)	C_{a6}–C_{m3}	1.399(3)	C_7–C_8	1.390(4)	C_{24}–C_{19}	1.375(4)
N_2–C_{a4}	1.377(3)	C_{a7}–C_{m3}	1.396(3)	C_8–C_9	1.392(5)	Mn_1–O_1	2.252(2)
N_3–C_{a5}	1.387(3)	C_{a5}–C_{m4}	1.391(3)	C_9–C_{10}	1.375(5)	Mn_2–O_2	2.270(2)
N_3–C_{a6}	1.377(3)	C_{a8}–C'_{m4}	1.386(3)	C_{10}–C_{11}	1.367(5)	O_1–C_{25}	1.424(5)
N_4–C_{a7}	1.381(3)	C_{b1}–C_{b2}	1.349(4)	C_{11}–C_{12}	1.391(5)	O_2–C_{26}	1.391(6)
N_4–C_{a8}	1.390(3)	C_{b3}–C_{b4}	1.348(4)	C_{12}–C_7	1.381(4)	O_3–C_{27}	1.366(15)
C_{a1}–C_{b1}	1.426(4)	C_{b5}–C_{b6}	1.346(4)	C_{13}–C_{14}	1.381(4)	Cl–O_4	1.402(5)
C_{a2}–C_{b2}	1.426(4)	C_{b7}–C_{b8}	1.345(4)	C_{14}–C_{15}	1.385(4)	Cl–O_5	1.386(6)
C_{a3}–C_{b3}	1.424(4)	C_{m1}–C_1	1.493(4)	C_{15}–C_{16}	1.378(4)	Cl–O_6	1.375(6)
C_{a4}–C_{b4}	1.434(4)	C_{m2}–C_7	1.508(4)	C_{16}–C_{17}	1.360(5)	Cl–O_7	1.415(7)
C_{a5}–C_{b5}	1.429(3)	C_{m3}–C_{13}	1.494(3)	C_{17}–C_{18}	1.388(5)		
C_{a6}–C_{b6}	1.434(3)	C_{m4}–C_{19}	1.514(3)				

a) Primed (′) atoms are related to unprimed atoms by the symmetric transformation.

TABLE 3. SELECTED INTERATOMIC ANGLES FOR $\mathrm{MnTPP(CH_3OH)_2\ ClO_4CH_3OH}$[a)]

Bond angle	$\phi/°$		$\phi/°$	Bond angle	$\phi/°$		$\phi/°$
$\mathrm{N_1{-}Mn_1{-}N_2}$	90.3(2)	$\mathrm{C_{a3}{-}C_{b3}{-}C_{b4}}$	107.4(3)	$\mathrm{C_1{-}C_{m1}{-}C'_{a4}}$	117.3(2)	$\mathrm{C_{10}{-}C_{11}{-}C_{12}}$	119.7(3)
$\mathrm{N_1{-}Mn_1{-}N'_2}$	89.7(2)	$\mathrm{C_{a4}{-}C_{b4}{-}C_{b3}}$	107.7(3)	$\mathrm{C_1{-}C_{m1}{-}C_{a1}}$	118.7(2)	$\mathrm{C_{11}{-}C_{12}{-}C_7}$	120.5(3)
$\mathrm{N_3{-}Mn_2{-}N_4}$	89.8(2)	$\mathrm{C_{a5}{-}C_{b5}{-}C_{b6}}$	107.2(2)	$\mathrm{C_7{-}C_{m2}{-}C_{a2}}$	118.0(2)	$\mathrm{C_{18}{-}C_{13}{-}C_{14}}$	119.1(2)
$\mathrm{N_3{-}Mn_2{-}N'_4}$	90.3(2)	$\mathrm{C_{a6}{-}C_{b6}{-}C_{b5}}$	107.8(2)	$\mathrm{C_7{-}C_{m2}{-}C_{a3}}$	117.3(2)	$\mathrm{C_{13}{-}C_{14}{-}C_{15}}$	120.2(3)
$\mathrm{Mn_1{-}N_1{-}C_{a1}}$	127.2(2)	$\mathrm{C_{a7}{-}C_{b7}{-}C_{b8}}$	107.5(2)	$\mathrm{C_{13}{-}C_{m3}{-}C_{a6}}$	116.8(2)	$\mathrm{C_{14}{-}C_{15}{-}C_{16}}$	120.3(3)
$\mathrm{Mn_1{-}N_1{-}C_{a2}}$	126.8(2)	$\mathrm{C_{a8}{-}C_{b8}{-}C_{b7}}$	107.7(2)	$\mathrm{C_{13}{-}C_{m3}{-}C_{a7}}$	119.3(2)	$\mathrm{C_{15}{-}C_{16}{-}C_{17}}$	119.7(3)
$\mathrm{Mn_1{-}N_2{-}C_{a3}}$	126.7(2)	$\mathrm{N_1{-}C_{a1}{-}C_{m1}}$	125.7(2)	$\mathrm{C_{19}{-}C_{m4}{-}C_{a5}}$	116.3(2)	$\mathrm{C_{16}{-}C_{17}{-}C_{18}}$	120.4(3)
$\mathrm{Mn_1{-}N_2{-}C_{a4}}$	127.2(2)	$\mathrm{N_1{-}C_{a2}{-}C_{m2}}$	125.4(2)	$\mathrm{C_{19}{-}C_{m4}{-}C'_{a8}}$	119.5(2)	$\mathrm{C_{17}{-}C_{18}{-}C_{13}}$	120.4(3)
$\mathrm{Mn_2{-}N_3{-}C_{a5}}$	126.7(2)	$\mathrm{N_2{-}C_{a3}{-}C_{m2}}$	126.0(2)	$\mathrm{C_{m1}{-}C_1{-}C_2}$	119.9(3)	$\mathrm{C_{24}{-}C_{19}{-}C_{20}}$	119.0(3)
$\mathrm{Mn_2{-}N_3{-}C_{a6}}$	127.1(2)	$\mathrm{N_2{-}C_{a4}{-}C'_{m1}}$	125.9(2)	$\mathrm{C_{m1}{-}C_1{-}C_6}$	121.1(3)	$\mathrm{C_{19}{-}C_{20}{-}C_{21}}$	120.8(3)
$\mathrm{Mn_2{-}N_4{-}C_{a7}}$	127.4(2)	$\mathrm{N_3{-}C_{a5}{-}C_{m4}}$	126.1(2)	$\mathrm{C_{m2}{-}C_7{-}C_8}$	120.0(2)	$\mathrm{C_{20}{-}C_{21}{-}C_{22}}$	119.6(3)
$\mathrm{Mn_2{-}N_4{-}C_{a8}}$	126.9(2)	$\mathrm{N_3{-}C_{a6}{-}C_{m3}}$	126.2(2)	$\mathrm{C_{m2}{-}C_7{-}C_{12}}$	120.7(2)	$\mathrm{C_{21}{-}C_{22}{-}C_{23}}$	120.2(3)
$\mathrm{C_{a1}{-}N_1{-}C_{a2}}$	105.7(2)	$\mathrm{N_4{-}C_{a7}{-}C_{m3}}$	125.6(2)	$\mathrm{C_{m3}{-}C_{13}{-}C_{14}}$	121.3(2)	$\mathrm{C_{22}{-}C_{23}{-}C_{24}}$	121.1(3)
$\mathrm{C_{a3}{-}N_2{-}C_{a4}}$	106.1(2)	$\mathrm{N_4{-}C_{a8}{-}C'_{m4}}$	125.6(2)	$\mathrm{C_{m3}{-}C_{13}{-}C_{18}}$	119.6(2)	$\mathrm{C_{23}{-}C_{24}{-}C_{19}}$	119.3(3)
$\mathrm{C_{a5}{-}N_3{-}C_{a6}}$	105.9(2)	$\mathrm{C_{m1}{-}C_{a1}{-}C_{b1}}$	124.8(2)	$\mathrm{C_{m4}{-}C_{19}{-}C_{20}}$	119.2(2)	$\mathrm{N_1{-}Mn_1{-}O_1}$	89.4(2)
$\mathrm{C_{a7}{-}N_4{-}C_{a8}}$	105.7(2)	$\mathrm{C_{m2}{-}C_{a2}{-}C_{b2}}$	124.5(2)	$\mathrm{C_{m4}{-}C_{19}{-}C_{24}}$	121.8(2)	$\mathrm{N_2{-}Mn_1{-}O_1}$	89.7(2)
$\mathrm{N_1{-}C_{a1}{-}C_{b1}}$	109.6(2)	$\mathrm{C_{m2}{-}C_{a3}{-}C_{b3}}$	124.3(2)	$\mathrm{C_6{-}C_1{-}C_2}$	119.0(3)	$\mathrm{N_3{-}Mn_2{-}O_2}$	88.2(2)
$\mathrm{N_1{-}C_{a2}{-}C_{b2}}$	110.0(2)	$\mathrm{C_{m1}{-}C_{a4}{-}C_{b4}}$	124.6(2)	$\mathrm{C_1{-}C_2{-}C_3}$	120.8(3)	$\mathrm{N_4{-}Mn_2{-}O_2}$	87.8(2)
$\mathrm{N_2{-}C_{a3}{-}C_{b3}}$	109.6(2)	$\mathrm{C'_{m4}{-}C_{a5}{-}C_{b5}}$	124.2(2)	$\mathrm{C_2{-}C_3{-}C_4}$	119.6(4)	$\mathrm{Mn_1{-}O_1{-}C_{25}}$	124.6(3)
$\mathrm{N_2{-}C_{a4}{-}C_{b4}}$	109.2(2)	$\mathrm{C_{m3}{-}C_{a6}{-}C_{b6}}$	124.5(2)	$\mathrm{C_3{-}C_4{-}C_5}$	120.9(4)	$\mathrm{Mn_2{-}O_2{-}C_{26}}$	124.0(3)
$\mathrm{N_3{-}C_{a5}{-}C_{b5}}$	109.7(2)	$\mathrm{C_{m3}{-}C_{a7}{-}C_{b7}}$	124.8(2)	$\mathrm{C_4{-}C_5{-}C_6}$	119.2(4)	$\mathrm{O_4{-}Cl{-}O_5}$	111.1(3)
$\mathrm{N_3{-}C_{a6}{-}C_{b6}}$	109.4(2)	$\mathrm{C'_{m4}{-}C_{a8}{-}C_{b8}}$	124.9(2)	$\mathrm{C_5{-}C_6{-}C_1}$	120.6(3)	$\mathrm{O_4{-}Cl{-}O_6}$	114.5(3)
$\mathrm{N_4{-}C_{a7}{-}C_{b7}}$	109.5(2)	$\mathrm{C_{a1}{-}C_{m1}{-}C'_{a4}}$	123.8(2)	$\mathrm{C_{12}{-}C_7{-}C_8}$	119.4(3)	$\mathrm{O_4{-}Cl{-}O_7}$	105.6(4)
$\mathrm{N_4{-}C_{a8}{-}C_{b8}}$	109.6(2)	$\mathrm{C_{a2}{-}C_{m2}{-}C_{a3}}$	124.7(2)	$\mathrm{C_7{-}C_8{-}C_9}$	119.8(3)	$\mathrm{O_5{-}Cl{-}O_6}$	110.0(4)
$\mathrm{C_{a1}{-}C_{b1}{-}C_{b2}}$	107.9(2)	$\mathrm{C_{a6}{-}C_{m3}{-}C_{a7}}$	123.9(2)	$\mathrm{C_8{-}C_9{-}C_{10}}$	119.9(3)	$\mathrm{O_5{-}Cl{-}O_7}$	109.6(4)
$\mathrm{C_{a2}{-}C_{b2}{-}C_{b1}}$	106.8(2)	$\mathrm{C_{a5}{-}C_{m4}{-}C'_{a7}}$	124.3(2)	$\mathrm{C_9{-}C_{10}{-}C_{11}}$	120.8(3)	$\mathrm{O_6{-}Cl{-}O_7}$	104.7(4)

a) Primed (′) atoms are related to unprimed atoms by the symmetric transformation. The estimated standard deviations of the least significant digits are given in parentheses.

located at 0,0,0 and 1/2, 1/2, 0. A series of difference Fourier calculations phased with two Mn and several atoms of the porphyrin skeleton revealed the positions of all non-hydrogen atoms. Atomic scattering factors were taken from Table 2.2B of Ref. 17. After several cycles of block-diagonal least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms, difference Fourier maps revealed all hydrogen atom positions except those of the solvated methanol. These invisible hydrogens were ignored in this work. The 36 hydrogen atoms refined two cycles, then, placed on the positions as the fixed contributors with their isotropic thermal parameters.

The refinement was carried to convergence using anisotropic temperature factors for all non-hydrogen atoms. The final values of the discrepancy indexes were $R=\sum||F_o|-|F_c||/\sum|F_o|=0.063$ and $R_w=[\sum(w(|F_o|-|F_c|)^2)/\sum w(F_o)^2]^{1/2}=0.071$, $w=1/\sigma^2(F_o)$. The highest residual in the difference map, 1.1 e/Å^3, was found near one oxygen atom (O_4) of the perchlorate ion and others (less than 0.6 e/Å^3) were featureless. All calculations were carried out at the Computing Center of Nagoya City University using locally modified versions of the X-ray programs.[18)]

Tables of the anisotropic thermal factors of 61 non-hydrogen atoms, the coordinates and isotropic thermal factors of hydrogen atoms, the observed and calculated structure factors (29 pages), and Fig. 4[30)] are available as supplementary materials on request (kept at the Editorial Office of the Chemical Society of Japan as a Document No. 8301).

Results and Discussion

Atomic coordinates and the associated isotropic equivalent temperature factors of the final non-hydrogen atoms are listed in Table 1. Figures 1 and 4[30)] are computer-drawn models of the two unique $\mathrm{MnTPP(CH_3OH)_2^+}$ ions. The two Mn ions, the hydrogen bonds formed by the coordinated methanols with perchlorate ion and solvated methanol, and the nearest contacts to them are collectively illustrated in Fig. 2. Individual bond lengths and angles are summarized in Tables 2 and 3.

The requirement of the inversion symmetry with respect to both manganese positions leads to square bipyramidal coordination spheres made of the porphinato core and axial methanols with rigorous centering of the Mn(III) ions. The symbols and displacements of the atoms from the least-squares mean plane of the porphyrin core for both ions are given by means of the usual diagram expression[19)] in Fig. 3. This shows planar porphyrin core normally seen in the six-coordinate Mn(III)[20)] and iron(III) porphyrins.[19)]

The conformation of two independent $\mathrm{MnTPP(CH_3OH)_2^+}$ ions is apparently identical. The dihedral angles between the least-squares mean planes of porphyrin core (24 atoms) and peripheral phenyl rings are 84.4° and 75.2° for the molecule shown in Fig. 1 and 70.8° and 72.7° for the second molecule.[30)] These are normal dihedral angles observed in ordinary TPP conformation.[21)] The most crucial structural difference distinguishing the complexes is the geometry of ions, ligands, and solvated molecules linked by the hydrogen bonds. As seen in Fig. 2, one oxygen atom (O_4) of the

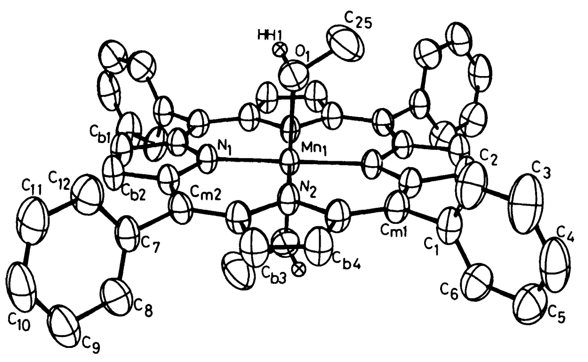

Fig. 1. Computer-drawn model of the first $MnTPP(CH_3OH)_2{}^+$ species. The thermal ellipsoids are contoured at the 50% probability level except for the hydrogen atom HH1.

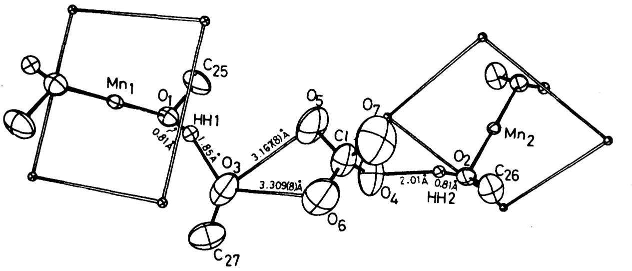

Fig. 2. An ORTEP plot of a pair of Mn(III)porphyrin ions and a perchlorate ion. The porphyrin planes are shown by simple squares linking the *meso*-carbons of the skeleton. Interatomic distances between perchlorate and solvated methanol oxygens and tentative distances between hydrogen and oxygen atoms forming hydrogen bonds are entered on the diagram.

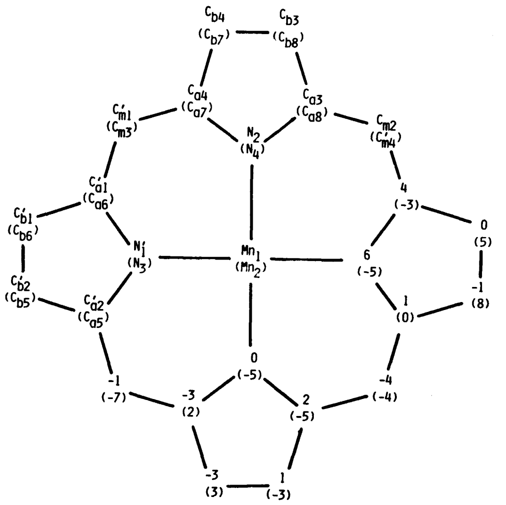

Fig. 3. A formal diagram of the porphinato core of the two unique Mn(III)porphyrins correspondings to Figs. 1 and 4[30] (in parentheses), respectively. On the upper left, the numbering scheme used for the atoms is displayed. The number on the atom positions in the centrosymmetric diagram, on the lower right, is the perpendicular displacement from the mean plane of the porphyrin core in units of 0.01 Å.

perchlorate ion interacts directly with the oxygen (O_2) of methanol coordinated to Mn_2 through a hydrogen bond (O_4–O_2 distance 2.798(5) Å). On the other side, the perchlorate ion has a close contact only with the solvated methanol at 3.16 Å that is too far for significant hydrogen bonding. The solvated methanol makes a dimeric interaction with the methanol coordinated to Mn_1 through an apparent hydrogen bond (O_1–O_3 distance 2.618(7) Å). Therefore, the crystal structure suggests a better description of the molecules in the solid state as $[MnTPP((CH_3OH)_2)_2]^+$ and $[MnTPP(CH_3OH \cdot ClO_4)_2]^-$ forming an ion pair. However, the description is not necessarily or strictly adapted to the present system because of the possible disorder suggested by the large thermal parameters and the high residual electron densities around the perchlorate and solvated methanol.

The ion pair makes a quasi-linear arrangement parallel to the (a—b) vector on the (0,0,1) plane; hence two manganese atoms sitting at 0,1,0 and 1/2,1/2,0 can be linked as shown in Fig. 2. The closest distance between two manganese atoms sitting on the quasi-chain is 9.3 Å. The dihedral angle between the two independent porphyrin planes is 51.8°.

The axial bond length of Mn_1–O_1 and Mn_2–O_2 are 2.252(2) Å (in the cationic species) and 2.270(2) Å (in the anionic species), respectively. These distances are considerably longer than the 2.11—2.16 Å values found in $[FeOEP(C_2H_5OH)_2]^+$[8] and $[FeTPP(C_2H_5OH)_2]^+$[22] in which both Fe(III) ions are assigned to be high-spin, but fairly shorter than 2.329(7) Å in $MnTPP(N_3)(CH_3OH)$.[20] The distances are comparable rather to the longer pair of Mn–N (imidazolate) bond lengths (2.280 (4) Å) in $(MnTPP(Im))_n$[23] or the value 2.308(3) Å found in the high-spin $MnTPP(1\text{-}MeIm)_2ClO_4$[24] in spite of the weak ligating nature of alcohol to metals. Axial bond lengths of high-spin Mn(III) porphyrin complexes are unexceptionally long (>2.2 Å) compared with normal equatorial Mn–N (porphyrin) bond lengths (*vide infra*). The difference between the axial bond lengths in the two independent species is statistically significant but substantially not distinct, since the 0.018 Å difference is small and considered to be due to the subtle electrostatic or crystal packing effect.

The average equatorial bond length (Mn–N(porphyrin)) in these ions is 2.006(2) Å, which is at the short limit of those found in four six-coordinate Mn(III) porphyrins; 2.009(9) Å in $MnTPP(Cl)(Py)$,[25] 2.015(4) Å in $MnTPP\,(1\text{-}MeIm)_2ClO_4$,[24] 2.019(4) Å in $(MnTPP\,(Im))_n$,[23] and 2.031(12) Å in $MnTPP(N_3)(CH_3OH)$.[20] The present average length of Mn–N is located at the middle of the extent of the equatorial bond lengths (1.93—2.09 Å) observed for a series of the first row transition metal-porphyrins.[29] Thus, the long axial bonds to methanol and medium size porphyrin core surround the high-spin Mn(III) ions. These structural characteristics in the six-coordinate high-spin Mn(III) porphyrins have already been pointed out as the tetragonal distortion found in those complexes.[20,23,25]

We are interested in the spin state/structure relationship of metalloporphyrins, especially biologically important iron porphyrins. Spin states of the central metal

TABLE 4. THE STRUCTURE-ELECTRONIC CONFIGURATION IN SELECTED SIX-COORDINATE METALLOPORPHYRINS HAVING ONE ELECTRON IN THE e_g ORBITAL

Number of electrons in 3d-orbital	Electronic configuration and spin state	Metalloporphyrins	Bond length of metal to axial ligand l/Å	Average bond length of metal to porphyrin l/Å	Ref.
4	$(t_{2g})^3(e_g)^1$	$MnTPP(CH_3OH)_2^+$	2.250(2) 2.272(2)	2.006(2)	This work
	$S=4/2$	$MnTPP(1\text{-}MeIm)_2^+$	2.308(3)	2.009(9)	24
		$(MnTPP(Im))_n^{a)}$	2.280(4)	2.019(4)	23
5	$(t_{2g})^4(e_g)^1$ $S=3/2$	$(FeTPP(C(CN)_3))_n$	2.317(3)	1.995(3)	12
6	$(t_{2g})^5(e_g)^1$ $S=2/2$	Unknown			
7	$(t_{2g})^6(e_g)^1$	$CoTPP(Pip)_2^{b)}$	2.436(2)	1.987(2)	27
	$S=1/2$	$CoOEP(\beta\text{-}Pic)_2^{b)}$	2.386(2)	1.992(1)	28

a) The high-spin form. b) Abbreviations: Pip=piperidine, OEP=octaethylporphinato, and β-Pic=3-methylpyridine.

ions define the distribution of electrons in the 3d-orbitals. The high-spin manganese(III) has an electron population in the 3d-orbitals of $(d_{xy},d_{yz},d_{zx})^3(d_{z^2})^1(d_{x^2-y^2})^0$ or $(t_{2g})^3(e_g)^1$ in the expression of cubic symmetry. The structures of the metalloporphyrins with similar electron configuration and six-coordinate geometry are compared and summarized in Table 4. The presence of a single electron in the e_g orbitals leads to a structural similarity, *i.e.*, tetragonal distortion. The addition of electrons into half-occupied t_{2g} orbitals –spin-pairing– appears to give only minor changes in the structural prameters of the porphyrin core, *i.e.*, metal to porphyrin bond lengths.

For the six-coordinate intermediate-spin iron(III) porphyrin, a true 3/2 spin-state has been suggested[12] as distinguished from a quantum mechanically admixed $S=3/2$, 5/2 state postulated for the five-coordinate iron(III) complexes.[11,13] The comparison of the structural parameters in Table 4 including the present Mn(III) porphyrins gives a stereochemical support for the assignment of the $S=3/2$ ground state electron configuration of the six-coordinate $FeTPP(C(CN)_3)$ in the solid state, despite of the higher than expected value of the observed magnetic moment. The magnetic properties may be elucidated by various experimental and theoretical ascriptions such as the thermal "spin-equilibrium" or the admixture of the excited state with the ground state configuration as has been adapted to the low-spin hemes.[26] We wish to remark conclusively that the present structure will contribute not only to the coordination chemistry of methanol to Mn(III) porphyrins but also to the electronic state consideration of related metalloporphyrins.

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6) Abbreviations: TPPS = *meso*-tetra (*p*-sulfophenyl) porphinato; TPP=*meso*-tetraphenylporphinato; DMSO=dimethyl sulfoxide; TMS=tetramethylsilane; Im=imidazolate; 1-MeIm=1-methylimidazole; Py=pyridine.

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30) Figure 4 displays the same information about the second molecule as in Fig. 1. The computer-drawn model is kept at the office of the Chemical Society of Japan as a supplementary material according to the editors' suggestion.