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Crystal and Molecular Structure of Unsymmetrical *N*-Methyl-substituted μ-Oxo Diiron(III) Tetraphenylporphyrin

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Abstract

The complex [(NCH$_3$TPP)Fe^{III}–O–Fe^{III}(TPP)]-ClO$_4$, where TPP is the dianion of *meso*-tetraphenylporphyrin and NCH$_3$TPP is the monoanion of *N*-methyl-*meso*-tetraphenylporphyrin, has been characterized by single-crystal X-ray structure analysis.

The compound crystallizes in the space group $P2_1/c$ with cell dimensions (133 K) of a = 16.605(5), b = 16.827(3), c = 28.075(9) Å, β = 105.30(2)° with Z = 4. The structure has been refined to an R index on F of 0.074 on the basis of 8396 reflections (Mo Kα).

The discrete (NCH$_3$TPP)Fe^{III}–O– unit exhibits a highly distorted square pyramidal coordination about iron(III) with the oxo ligand occupying the apical position (Fe(2)–O(1) = 1.740(4) Å). The *N*-methylated porphyrin ligand forms three strong bonds to iron(III) (Fe(2)–N(121) = 2.053(5) Å; Fe(2)–N(122) = 2.055(6) Å; Fe(2)–N(124) = 2.066(6) Å) together with a weaker one (Fe(2)–N(123) = 2.257(5) Å) between the methylated nitrogen atom and the iron(III) atom. The Fe^{III} displacement above the N(121), N(122), N(124) reference plane is 0.526(2) Å and the dihedral angles between pyrrole rings and the reference plane are: *N*-methylated 33.1(2)°, opposite 5.1(2)°, adjacents –12.3(2)° and –13.2(2)°. The first example of ferric ion coordination by *N*-methylporphyrin has been compared to the ferrous analogue.

The discrete (TPP)Fe^{III}–O– unit exhibits a square pyramidal coordination with an apical position of the oxo ligand Fe(1)–O(1) = 1.767(4) Å) and the average Fe(1)–N bond length in the range characteristic for high-spin ferric porphyrins (Fe(1)–N$_{av}$ = 2.066(6) Å). The Fe(1)–O(1)–Fe(2) angle is distinctly non-linear with a value 165.4(3)° due to the steric interaction imposed by the *N*-methylated pyrrole ring. The facing porphyrins are twisted by 30.2(2)° with respect to one another.

Introduction

The routes to the physiological formation of N-substituted porphyrins [1–3] have been probed by extensive model studies of iron N-substituted porphyrins [4–15]. In general iron N-substituted porphyrins are expected to play an important role in the metallorganic chemistry of iron porphyrins [16]. The major differences in the structures of metal complexes of N-substituted and non-N-substituted porphyrins are: the unique bond to the *N*-methyl-substituted nitrogen, out-of-plane displacement of the metal atom and considerable tilting of the *N*-methylated pyrrole ring [17]. Complexation with N-substituted porphyrin stabilizes the iron(II) oxidation state relative to iron(III) [4, 5, 12]. One electron oxidation of iron(II) N-substituted porphyrins has been accomplished electrochemically and followed by UV–Vis spectroscopy [12]. Ogoshi *et al.* reported the synthesis of monomeric iron(III) *N*-methyloctaethylporphyrin by a procedure similar to that used for the synthesis of iron(II) *N*-methylporphyrins [10]. Mansuy *et al.* presented evidence for the formation of iron(III) *N*-alkylporphyrins involving five-membered Fe–O–C–C–N metallocycles [13]. Chemical oxidation of iron(II) *N*-methylporphyrins was followed by ^{1}H NMR and the respective products, i.e. iron(III) *N*-methylporphyrins, were characterized in solution in low temperature conditions [9]. Recently we have shown that the use of a moderate oxidant (AgClO$_4\cdot$3CH$_3$CN) resulted in the formation of two μ-oxo bridged diiron(III) complexes: symmetrical [(NCH$_3$TPP)Fe^{III}–O–Fe^{III}-(NCH$_3$TPP)](ClO$_4$)$_2$ and unsymmetrical [(NCH$_3$TPP)-Fe^{III}–O–Fe^{III}(TPP)]ClO$_4$ [18].

In this paper we wish to present the molecular structure of the unsymmetrical μ-oxo bridged diiron(III) porphyrin system. This is the very first structural characterization of iron(III) N-substituted porphyrin which offers a quite unique chance to make a direct analysis of one electron metal-centered oxidation influence on structural parameters in N-substituted

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metalloporphyrins. Although many structures of divalent metal *N*-alkylporphyrins are known, there is apparently no example in the literature of a fully structurally characterized molecule containing a trivalent metal ion *N*-alkylporphyrin moiety [17]. In addition, the studied complex is one of the very rare examples of a μ-oxo bridged diiron(III) system where each iron is located in a substantially different coordination sphere [19].

Experimental

$[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]ClO_4 \cdot CH_2Cl_2$ was synthesized as described previously [18]. The crystals were grown by diffusion of hexane into a dichloromethane solution of the complex.

Space group $P2_1/c$ was determined from oscillation and Weissenberg photographs and unambiguously defined from systematic absences.

An initial set of diffraction data was collected at room temperature on a CAD-4 single-crystal automated diffractometer using Cu Kα graphite-monochromated ($\lambda = 1.54178$ Å) radiation in the Chemical Crystallography Laboratory, Oxford University, U.K. A crystal of dimensions 0.08 × 0.15 × 0.25 was used for data collection in the ω–2θ mode. A total of 4690 unique reflections with $2\theta \leqslant 80°$ was collected of which 1908 having $F_o{}^2 > 2\sigma(F_o{}^2)$ were retained as observed. Lattice constants: $a = 16.685(3)$, $b = 17.188(4)$, $c = 28.110(6)$ Å, $\beta = 105.30(2)°$. The structure was solved by the direct methods [20] and the solution demonstrated two irons and the bridging oxygen together with a large portion of the porphyrin cores. The subsequent calculations were performed with the CRYSTALS crystallographic program [21] on a VAX11/750 computer. The remaining atoms were found by difference Fourier syntheses and full-matrix least-squares refinement. Positions of some terminal carbon atoms belonging to the phenyl rings were calculated geometrically. At this stage, the carbon atom C(45) of the methyl group bonded to N(123) was found from the difference Fourier synthesis. Since the ratio of number of parameters to number of reflections was very unfavourable (*c*. 4.5 in the isotropic case), the structure could not be refined in the usual way. Therefore the technique of soft constraints [21] was employed using bond lengths found for μ-oxo-bis-[(5, 10, 15, 20-tetraphenylporphinato)iron(III)] by Swepston and Ibers [22]. The final *R* factor was 0.143 for 376 parameters. At this stage attempts were undertaken to grow larger crystals to collect a more extensive set of data.

A second set of data was collected at –140 °C on a CAD-4 diffractometer in Łódź using Mo Kα graphite monochromated radiation ($\lambda = 0.71069$ Å). Data collection parameters are given in Table 1. An absorption correction based on ψ scans was applied. The existing set of atomic parameters obtained for Cu Kα data was used for refinement with Mo Kα data set on an AMSTRAD 1512 SD personal computer using the SHELX76 systems of programs [23].

TABLE 1. Crystallographic data

Formula	$C_{89}H_{59}ClN_8O_5Fe_2 \cdot CH_2Cl_2$
Molecular weight	1551.43
Color and habit	dark purple prisms
Crystal system	monoclinic
a (Å)	16.605(5)
b (Å)	16.827(3)
c (Å)	28.075(9)
β (°)	105.30(2)
V (Å^3)	7566(4)
Z	4
D_{obs} (flotation in aq. KI)	1.36
D_{calc} (g cm^{-3})	1.361
μ (cm^{-1}) Mo Kα	5.0
$F(000)$	3200
Crystal dimensions (mm)	0.52 × 0.64 × 0.68
Space group	$P2_1/c$
Scan mode	ω–2θ
Scan angle (°)	1.2
Scan speed (° mm^{-1})	variable
Max. 2θ (°)	50
No. data measured	16396
No. data with $F_o > 4\sigma(F_o)$	8398
Abs. max./min.	1.19/0.98
R	0.074

Refinements were carried out using blocked full-matrix technique [23] on *F* to convergence employing anisotropic temperature factors for all non-hydrogen atoms. The final value of *R* was 0.074 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_c|$).

Unit weights were used as the weighting scheme $1/\sigma^2$ did not work satisfactorily. Hydrogen atoms were included into the structure factor calculations but no hydrogen atom was allowed to vary during the refinement. A final difference map showed no significant maxima. The scattering factors and anomalous dispersion coefficients were taken from refs. [24] and [25] respectively. In addition to SHELX76 [23], XANADU [26], PARST [27] and CSU [28] programs were used.

Results and Discussion

An overall view of the $[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]^+$ cation is given in Fig. 1. Figure 2 presents two different moieties of the studied complex, i.e. $(NCH_3TPP)Fe^{III}$– and $(TPP)Fe^{III}$–O– and gives the labels assigned to each atom. Tables 2 and 3 present a listing of fractional coordinates and selected individual bond distances and angles. As

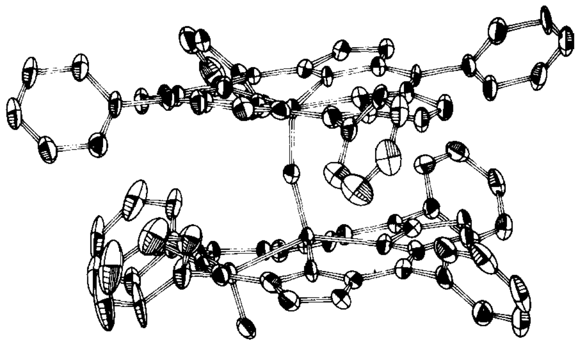

Fig. 1. The $[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]^+$ cation (50% ellipsoids shown). Hydrogen atoms are omitted.

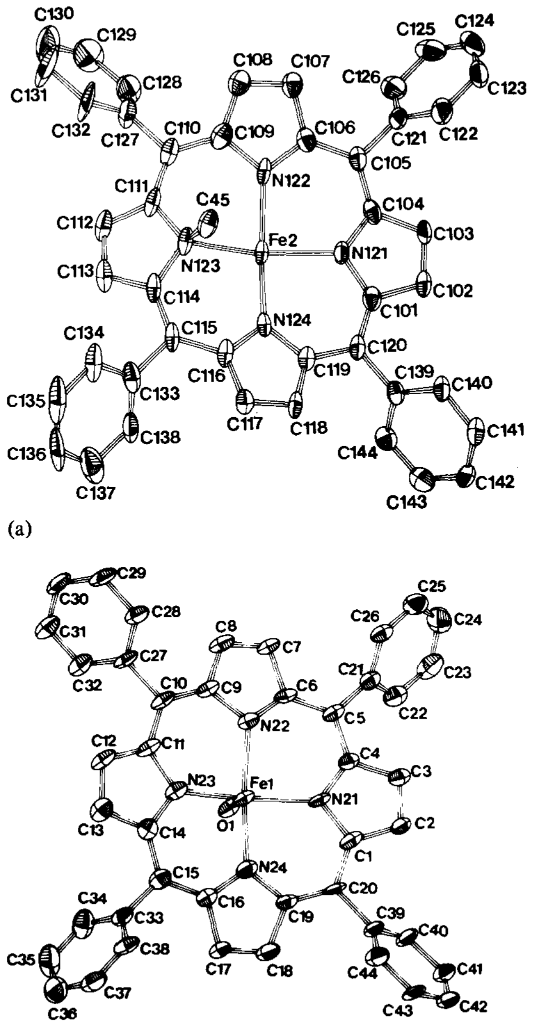

Fig. 2. Computer drawn models and numbering scheme for (a) $(NCH_3TPP)Fe^{III}–$ and (b) $(TPP)Fe^{III}–O–$ fragments of $[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]ClO_4$. Ellipsoids are scaled at the 50% probability level.

expected the structure bears similarities to those reported previously for μ-oxo bridged diiron(III) porphyrins: μ-oxo-bis((5,10,15,20-tetraphenylporphyrinato)iron(III)) $[(TPP)Fe]_2O$ [22, 29]; $Fe_2(\mu\text{-}O)FF\cdot H_2O$ (FF is confacial biporphyrin tetraanion) [30]; μ-oxo-bis((5,15-dimethyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)iron(III)) $[(ODM)Fe]_2O$ [31]; μ-oxo-bis((7,8-dihydro-5,10,15,20-tetraphenylporphyrinato)iron(III)) $[(TPC)Fe]_2O$ [32]; μ-oxo-bis((5,10,15,20-tetrakispentafluorophenylporphyrinato)iron(III)) $[(TPP(F_5)Fe]_2O$ [33] and $[(PPIXDME)Fe]_2O$ (PPIDME = protoporphyrin IX dimethyl ester dianion) [34].

However the intrinsic asymmetry of $[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]^+$ clearly distinguishes this molecule in the class of μ-oxo bridged diiron(III) porphyrins and locates this compound in the not quite so numerous group of biological and non-biological diiron systems where the stereochemistry about two irons is significantly different [19]. For the sake of simplification we intend to discuss the subtle structural differences between the following fragments of $[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]^+$: $(NCH_3TPP)Fe^{III}–$, $(TPP)Fe^{III}–O–$ and similar units found in $(NCH_3TPP)Fe^{II}Cl$ [4] and $[(TPP)Fe]_2O$ [22]. The $(TPP)Fe^{III}–O–$ moiety, as expected for high-spin ferric porphyrins, has a square pyramidal coordination sphere. Close adherence of this moiety to four-fold symmetry is evident in the small estimated deviation of the average core parameters ($Fe(1)–N_{av} = 2.066(6)$ Å). Fe(1)–N bond lengths are in the short end of the high-spin ferric porphyrins [35]. The average Fe(1)–N bond length is similar to those determined for $[(TPP)Fe]_2O$ (2.081(3) Å) [22] and $[(ODM)Fe]_2O$ (2.065(4)) [31]. Bond lengths and angles of TPP are identical for both compared diiron complexes. The perpendicular displacements of atoms in units of 0.01 Å from the 24-atom plane are: C1 21, C2 41, C3 31, C4 6, C5 −15, C6 −18, C7 −43, C8 −33, C9 −5, C10 10, C11 19, C12 43, C13 34, C14 7, C15 −13, C16 −22, C17 −43, C18 −35, C19 −10, C20 11, N21 4, N22 2, N23 1, N24 −6. The pyrrole rings are displaced alternately above and below the mean plane of the porphyrine core. S_4 ruffling twists each pyrrole ring and its attached pair of *meso* carbons about an axis through its nitrogen and the midpoint of the $C_\beta–C_\beta$ bond. Opposite pyrrole rings twist in opposite directions. The 0.43(2) Å displacement of the iron(III) from the mean porphyrin plane and the 0.44(2) Å displacement from the N_4 plane is usual for high-spin ferric porphyrins but slightly smaller than that found for $[(TPP)Fe]_2O$ (0.53(1) and 0.49(1) Å respectively) [22]. In general, the structural parameters of the $(TPP)Fe^{III}–$ unit are similar to $[(NCH_3TPP)Fe^{III}–O–Fe^{III}(TPP)]^+$ and $[(TPP)Fe]_2O$. The observed differences reflect some influence of the second moieties (an axial ligand effect).

TABLE 2. Atomic coordinates in the unit cell

Atom	Coordinates^a			
	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$	$10^3 \times U_{eq}$ (Å^2)
C11^b	2195(1)	2072(1)	5537(1)	55(0)
O2	2839(12)	2275(13)	5944(7)	104(6)
O2*	2707(27)	2385(23)	5952(12)	124(12)
O3	2401(14)	2099(11)	5097(7)	111(7)
O3*	2909(13)	1575(17)	5366(8)	109(8)
O4	1593(6)	2768(6)	5549(4)	58(3)
O4*	1899(18)	2458(20)	5098(9)	117(10)
O5	1721(4)	1420(4)	5627(2)	67(2)
C145	2642(9)	−636(7)	3167(5)	102(4)
C12	1998(7)	−55(9)	3411(6)	142(5)
C12*	2082(5)	−672(5)	3636(4)	155(3)
C13	2136(4)	−556(2)	2536(2)	171(2)
Fe1^c	7133(1)	2202(1)	2403(0)	27(0)
N21	5935(4)	2452(3)	1995(2)	30(2)
N22	6775(3)	2562(3)	3023(2)	29(1)
N23	8337(4)	2499(3)	2771(2)	31(1)
N24	7482(4)	2336(3)	1749(2)	31(1)
C1	5616(5)	2492(4)	1477(2)	31(2)
C2	4738(4)	2610(4)	1353(2)	30(2)
C3	4507(5)	2605(4)	1785(2)	33(2)
C4	5257(4)	2496(4)	2177(2)	29(2)
C5	5255(4)	2439(4)	2684(2)	30(2)
C6	5988(4)	2460(4)	3064(2)	29(2)
C7	6005(4)	2378(4)	3590(2)	31(2)
C8	6808(5)	2455(4)	3842(2)	37(2)
C9	7309(4)	2574(4)	3500(2)	32(2)
C10	8165(5)	2666(4)	3614(2)	34(2)
C11	8653(5)	2669(4)	3280(2)	33(2)
C12	9524(5)	2811(4)	3382(2)	37(2)
C13	9772(5)	2698(4)	2960(3)	38(2)
C14	9020(4)	2493(4)	2585(2)	32(2)
C15	9010(4)	2320(4)	2089(2)	32(2)
C16	8278(4)	2229(4)	1714(2)	32(2)
C17	8257(5)	2036(4)	1199(2)	36(2)
C18	7457(5)	2061(5)	941(3)	39(2)
C19	6960(4)	2260(4)	1277(2)	31(2)
C20	6104(4)	2379(4)	1146(2)	33(2)
C21	4437(4)	2358(4)	2790(2)	30(2)
C22	3897(5)	1735(5)	2589(3)	39(2)
C23	3136(5)	1646(5)	2672(3)	50(3)
C24	2894(5)	2169(6)	3000(3)	56(3)
C25	3402(5)	2785(5)	3201(3)	48(2)
C26	4166(5)	2883(4)	3102(2)	35(2)
C27	8629(5)	2735(4)	4157(2)	36(2)
C28	8384(5)	3326(5)	4444(3)	39(2)
C29	8795(5)	3373(5)	4951(3)	44(2)
C30	9437(5)	2863(5)	5165(3)	46(2)
C31	9680(5)	2285(5)	4882(3)	47(2)
C32	9272(5)	2221(5)	4380(3)	40(2)
C33	9818(4)	2227(4)	1963(2)	33(2)
C34	10336(5)	1594(5)	2142(3)	48(2)
C35	11056(5)	1458(6)	1999(4)	63(3)
C36	11273(6)	1972(6)	1661(3)	60(3)
C37	10766(5)	2613(5)	1490(3)	46(2)
C38	10050(5)	2745(4)	1637(2)	39(2)
C39	5651(4)	2390(4)	602(2)	34(2)
C40	4980(5)	1898(5)	404(3)	41(2)

(continued)

TABLE 2. *(continued)*

Atom	Coordinates[a]			
	$10^4 \times x$	$10^4 \times y$	$10^4 \times z$	$10^3 \times U_{eq}$ (Å^2)
C41	4537(5)	1955(5)	−99(3)	48(2)
C42	4787(6)	2501(5)	−402(3)	49(3)
C43	5478(5)	2971(5)	−211(2)	47(2)
C44	5906(5)	2933(5)	293(3)	42(2)
O1	7113(3)	1161(3)	2481(1)	31(1)
Fe2[d]	7045(1)	136(1)	2394(0)	28(0)
N121	6740(3)	−132(3)	1654(2)	29(1)
N122	8251(4)	−198(3)	2435(2)	32(2)
N123	7361(4)	−276(3)	3186(2)	32(2)
C45	7361(5)	−1164(4)	3096(2)	37(2)
N124	5837(3)	−158(3)	2394(2)	28(1)
C101	5954(4)	−53(4)	1348(2)	30(2)
C102	6035(5)	1(4)	840(2)	33(2)
C103	6833(4)	−87(4)	858(2)	34(2)
C104	7295(4)	−179(4)	1374(2)	30(2)
C105	8149(4)	−305(4)	1543(2)	32(2)
C106	8606(4)	−343(4)	2052(2)	32(2)
C107	9483(5)	−479(4)	2219(2)	34(2)
C108	9692(5)	−394(4)	2723(3)	37(2)
C109	8935(4)	−221(4)	2849(3)	34(2)
C110	8889(4)	−41(4)	3335(2)	34(2)
C111	8161(4)	19(4)	3468(2)	34(2)
C112	8023(5)	413(4)	3889(2)	43(2)
C113	7205(5)	373(4)	3876(2)	41(2)
C114	6771(5)	−39(4)	3449(2)	34(2)
C115	5915(5)	−159(4)	3280(2)	34(2)
C116	5475(5)	−285(4)	2780(2)	31(2)
C117	4613(4)	−456(4)	2609(2)	34(2)
C118	4418(5)	−398(4)	2105(2)	34(2)
C119	5168(4)	−193(4)	1979(2)	30(2)
C120	5214(4)	−77(4)	1478(2)	30(2)
C121	8642(5)	−413(4)	1175(2)	36(2)
C122	8460(6)	−1056(5)	842(3)	49(2)
C123	8945(6)	−1144(7)	505(3)	65(3)
C124	9573(7)	−633(8)	497(3)	74(4)
C125	9741(5)	12(6)	807(3)	60(3)
C126	9270(5)	115(5)	1155(3)	47(2)
C127	9678(5)	158(5)	3716(3)	45(2)
C128	10193(5)	757(5)	3629(3)	52(2)
C129	10912(6)	971(7)	3992(4)	73(3)
C130	11106(7)	571(9)	4447(4)	107(5)
C131	10613(7)	−29(10)	4528(4)	109(6)
C132	9876(6)	−241(7)	4169(3)	76(4)
C133	5422(5)	−77(5)	3650(3)	39(2)
C134	5651(6)	−557(5)	4080(3)	53(3)
C135	5182(8)	−512(7)	4419(3)	78(4)
C136	4513(8)	−41(8)	4342(3)	75(4)
C137	4288(7)	471(7)	3930(4)	73(3)
C138	4761(5)	428(5)	3576(3)	47(2)
C139	4399(4)	−31(4)	1094(2)	29(2)
C140	4173(5)	−623(4)	731(2)	32(2)
C141	3406(5)	−579(5)	381(3)	41(2)
C142	2872(4)	38(5)	390(2)	41(2)
C143	3090(5)	633(4)	740(3)	40(2)
C144	3854(5)	585(4)	1094(3)	35(2)

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[a] Numbers in parentheses are e.s.d.s in the last significant figure. [b] For Cl1 U_{eq} = 0.0554(4) Å^2. [c] For Fe1 z = 0.24034(3), U_{eq} = 0.0269(4) Å^2. [d] For Fe2 z = 0.23938(3), U_{eq} = 0.0276(4) Å^2.

TABLE 3. Bond lengths and angles in the oxo bridge and the coordination group

Bond	Length (Å)	Bond	Length (Å)
Fe1–N21	2.060(5)	Fe2–N121	2.053(5)
Fe1–N22	2.072(6)	Fe2–N122	2.055(6)
Fe1–N23	2.055(5)	Fe2–N123	2.257(5)
Fe1–N24	2.079(6)	Fe2–N124	2.066(6)
Fe1–O1	1.767(4)	Fe2–O1	1.740(4)
Angle	Value (°)	Angle	Value (°)
N21–Fe1–N22	87.6(2)	N121–Fe2–N122	88.5(2)
N21–Fe1–N23	154.0(2)	N121–Fe2–N123	149.3(2)
N22–Fe1–N23	87.9(2)	N122–Fe2–N123	83.7(2)
N21–Fe1–N24	86.5(2)	N121–Fe2–N124	88.1(2)
N24–Fe1–N22	156.8(2)	N122–Fe2–N124	150.1(2)
N23–Fe1–N24	87.5(2)	N123–Fe2–N124	84.2(2)
O1–Fe1–N21	102.9(2)	O1–Fe2–N121	110.5(2)
O1–Fe1–N22	99.7(2)	O1–Fe2–N122	103.7(2)
O1–Fe1–N23	103.1(2)	O1–Fe2–N123	100.2(2)
O1–Fe1–N24	103.6(2)	O1–Fe2–N124	105.4(2)
Fe1–N21–C1	128.9(5)	Fe2–N121–C101	123.6(5)
Fe1–N21–C4	125.3(4)	Fe2–N121–C104	125.0(4)
Fe1–N22–C6	122.2(4)	Fe2–N122–C106	128.0(4)
Fe1–N22–C9	124.0(5)	Fe2–N122–C109	128.4(5)
Fe1–N23–C11	127.5(5)	Fe2–N123–C45	98.5(4)
Fe1–N23–C14	126.9(4)	Fe2–N123–C111	112.0(4)
Fe1–N24–C16	123.5(4)	C111–N123–C45	113.0(5)
Fe1–N24–C19	125.9(5)	C114–N123–C45	113.1(6)
Fe1–O1–Fe2	165.4(3)	Fe2–N123–C114	114.2(4)
		Fe2–N124–C116	131.1(4)
		Fe2–N124–C119	125.1(5)

The (NCH$_3$TPP)Fe^{III}– unit can be treated as a product of one-electron oxidation of (NCH$_3$TPP)-Fe^{II}Cl. The Fe(2)–N bonds of (NCH$_3$TPP)Fe^{III}– follow a pattern observed for divalent metal ion *N*-alkylporphyrins. The bond distance from the iron(III) to the nitrogen atom (N(121) opposite the methylated nitrogen atom (N(123)) is comparable (Fe(2)–N(121) = 2.053(5) Å) to bonds formed by two other non-methylated nitrogens to iron(III) (Fe(2)–N(122) = 2.055(6) Å; Fe(2)–N(124) = 2.066(6) Å). All these distances are in the range expected for high-spin ferric porphyrins [35] and are quite close to those determined in (TPP)Fe^{III}– in the same structure. The interaction between iron(III) and the methylated nitrogen is weaker than other Fe–N bonds as demonstrated by the Fe(2)–N(123) distance 2.257(5) Å. The oxidation of iron(II) to iron(III) results in systematic shortening of the iron–nitrogen bonds as follows: Fe(2)–N(122), 0.062 Å; Fe(2)–N(121), 0.029 Å; Fe(2)–N(124), 0.050 Å; Fe(2)–N(123), 0.072 Å.

Similar observations have been made for high-spin ferrous versus high-spin ferric non-N-substituted porphyrins [35]. The analogous shortening of the Fe–N bond distance for the most representative couple, i.e. (TPP)Fe^{III}Cl [36] and [(TpivPP)Fe^{II}Cl]$^-$ (TpivPP *meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$-pivalamidophenyl)porphyrin dianion) [37] equals 0.048 Å. The decrease of bond lengths can be accounted for by a shrinking of the *N*-methylporphyrin macrocylce (*vide infra*) and a smaller ionic radius of high-spin iron(III) as compared to high-spin iron(II) [35, 38] (0.79 versus 0.92 Å, respectively [39]). The displacement of iron(III) from the plane defined by the three unsubstituted nitrogen atoms (the N$_3$ plane, i.e. the standard reference plane for N-substituted metalloporphyrins [17]) equals 0.53(2) Å and is smaller than for iron(II) (0.62 Å [4]). The bond lengths and thus the effective delocalization pattern in the ligand part of (NCH$_3$-TPP)Fe^{III}– remain practically unaffected by oxidation of iron(II) to iron(III). Also the extent of sp^3 hybridization of *N*-methylated nitrogen seems to be unchanged. The perpendicular displacements of atoms in units of 0.01 Å from the 23-atom plane are: C101 –17, C102 48, C103 34, C104 11, C105 –11, C106 –24, C107 –48, C108 –42, C109 –16, C110 6, C111 12, C112 71, C113 63, C114 3, C115 –19, C116 –33, C117 –60, C118 –43, C119 –5, C120 –14, C45 –182, N121 14, N122 –7, N123 –34, N124 –4. Another aspect of the *N*-methylporphyrin structure is the relative rotation of the pyrrole ring about the C_α–C_m bond. In the case of $(NCH_3TPP)Fe^{III}$– the *N*-methylated ring is rotated to a greater extent, while the pyrrole ring, located opposite the methylated one, is rotated to a lesser extent but in the same direction. The rings adjacent to the methylated one are rotated in opposite direction. For all of the divalent metal ion *N*-methylporphyrins the three non-alkylated rings are rotated in the opposite direction to the methylated ring [17]. This geometrical factor is characterized at the best by the dihedral angle between the N_3 plane and the pyrrole planes. The values for $(NCH_3TPP)Fe^{II}$– [17] and $(NCH_3TPP)Fe^{III}$– are respectively:

N-methylated ring	36.6°	31.1(2)°
Opposed ring	−6.4°	5.1(2)°
Adjacent ring	−11.3°	−13.1(2)°
Adjacent ring	−9.8°	−12.3(2)°

The twist angle change of the opposed pyrrole ring reflects the fact that the *N*-methylporphyrin macrocycle can expand and contract its core to provide the optimal bond length for the Fe(III)/Fe(II) couple. This property allows accomodation of high-spin iron(III), the smallest ever metal ion complexed by *N*-methylporphyrin up to now [17]. One can describe the *N*-methylporphyrin configuration as the saddle-like type.

The Fe(1)–O–Fe(2) angle of 165.4(3)° departs appreciably from linearity as compared to other μ-oxo diiron porphyrins: $[(TPP)Fe]_2O$, 176.1(2)° [22]; $[(ODM)Fe]_2O$, 178.6(6)° [31]; $[(TPC)Fe]_2O$, 180° [32]; $[(TPP(F_5))Fe]_2O$, 178.4(5)° [33]; $[(PPIXDME)Fe]_2O$, 172.5° [34] but is close to the value determined for the more strained $Fe_2(\mu\text{-}O)FF\cdot H_2O$ 161.4(4)° [30] and is in the range for other μ-oxo diiron complexes [19].

The Fe–O bond lengths of 1.767(4) and 1.740(4) Å lie in the range previously observed [19, 22, 30–34]. Despite the very different coordination around the two iron(III) centers, the difference in the bond lengths, although significant, is small (0.027 Å).

The N_4 plane of TPP and the N_3 plane of NCH_3-TPP are not parallel to one another: the dihedral angle equals 7.3°. Both porphyrin skeletons are in a staggered conformation (Fig. 3). The angle of twisting N(121)–Fe(2)–Fe(1)–N(22) equals 30.2(2)°. The phenyl rings of the two moieties are close to being eclipsed. Dihedral angles of phenyl ring planes with the N_4 plane of $(TPP)Fe^{III}$–O are equal: 50.2(2)°, 47.6(2)°, 119.7(2)°, 130.2(2)°. The corresponding values for $(NCH_3TPP)Fe^{III}$– (the N_3 plane) are: 5.1(2)°, 167.7(2), 146.9(2)°, 13.1(2)°.

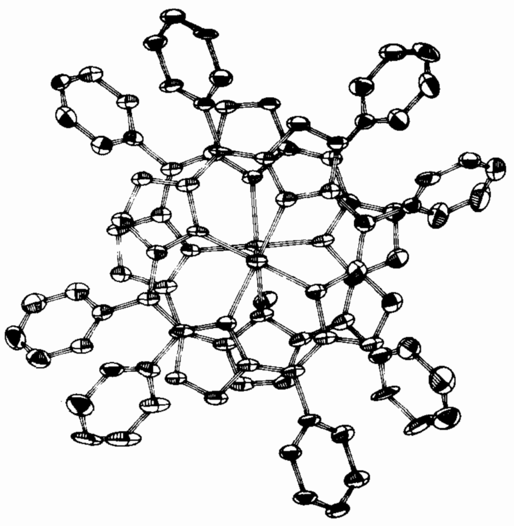

Fig. 3. Projection of $[(NCH_3TPP)Fe^{III}\text{–O–}Fe^{III}(TPP)]^+$ along the Fe(1)- - -Fe(2) axis.

The ClO_4^- ion is disordered. The site occupation factors of two alternative positions of O(2), O(3), O(4) and O(2*), O(3*), O(4*) were refined giving values of 0.62 and 0.38, respectively. The dichloromethane molecule is also disordered with the Cl(2) atom found in two positions, with occupation factors 0.36 and 0.64.

Conclusions

Our X-ray crystallographic studies demonstrated relatively small structural changes in μ-oxo diiron(III) porphyrin structures due to the replacement of tetraphenylporphyrin by *N*-methyltetraphenylporphyrin. The most considerable deformation, i.e. a decrease of the Fe–O–Fe angle to 165.4(3)° (−8.7°) results, in our opinion, from the steric interactions imposed by the *N*-methylated pyrrole ring. The tilting on the methyl porphyrin plane achieved in this way leads to an increase of the *N*-methylated pyrrole–TPP plane distance. Considerable similarities between ferric and ferrous *N*-methyltetraphenylporphyrin structures have been found.

Supplementary Material

Tables of structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available from the authors on request.

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