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Chloro(5,10,15,20-tetraphenylporphyrinato)manganese(III) with 4/*m* Symmetry

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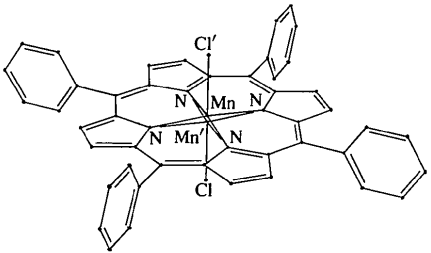
Abstract

The crystal structure of [Mn(TPP)Cl] in space group *I*4/*m* (where TPP is $C_{44}H_{28}N_4$) has been determined. The unit cell contains two full molecules, with one eighth of a molecule unique. An out-of-plane model for the Mn atom was applied and all non-H atoms were refined anisotropically. The Mn—N distance is 2.002 (3) Å, the axial Mn—Cl distance is 2.297 (15) Å and the out-of-plane displacement of the Mn atom is 0.16 Å. The possibility of a reverse-doming porphyrin core conformation is mentioned briefly.

Comment

For tetragonal [Mn(TPP)Cl] with required 4/*m* symmetry and a five-coordinate manganese(III) ion, the Mn and Cl atoms are required to be disordered along the axis at 0,0,±*z*. The coordination group distances that result are Mn—N = 2.002 (3), Ct···Cl = 2.452 (3), Mn—Cl = 2.297 (15) Å, and a Mn-atom displacement of ±0.16 Å.



[Mn(TPP)Cl]

These values are smaller than expected for a five-coordinate Mn^{III} porphyrinate. Indeed, in the crystal structure of [Mn(TPP)Cl] as the acetone solvate with no required symmetry for the molecule (Tulinsky & Chen, 1977), an axial Mn—Cl bond distance of 2.363 (3) Å, an average Mn—N bond length of 2.008 (15) Å and a Ct···Cl distance of 2.633 Å were observed; the Mn-atom displacement from the mean plane of the four N atoms was 0.27 Å. Essentially identical values were obtained for the chloroform solvate of [Mn(TPP)Cl] (Hoard, 1975). We believe that the coordination group parameters for the tetragonal form of [Mn(TPP)Cl] are underestimated and that this underestimation results from a reverse doming of the porphyrinato core that is caused by crystal packing and obscured by the crystallographically required 4/*m* symmetry. We note that a similar phenomenon is also observed in the structures of two crystal forms of [Fe(TPP)Cl] and [Zn(TPP)(H_2O)]. In the monoclinic form of [Fe(TPP)Cl] with no required symmetry, the axial Fe—Cl bond length is 2.211 (1) Å, the average Fe—N distance is 2.070 (9) Å and the Fe-atom displacement is 0.49 Å from the plane of the four N atoms (Scheidt & Finnegan, 1989). However, a set of significantly smaller values [2.192 (12), 2.049 (9) and 0.38 Å, respectively] were reported for the tetragonal structure with required 4/*m* symmetry (Hoard, Cohen & Glick, 1967). In addition, in the two Zn complexes, the tetragonal form (Glick, Cohen & Hoard, 1967; Golder, Povey, Silver & Jassim, 1990) has smaller coordination group parameters than the triclinic form (Cheng & Scheidt, 1995), although the comparison is made more difficult by the fact that the Zn—O(H_2O) bond is affected by strong hydrogen bonding to the aqua ligand in the triclinic form.

We note that there are many example of five-coordinate MTPP(*X*) complexes which crystallize in the space group *I*4/*m*; see Table XXVI of Scheidt & Lee (1987) for a number of examples.

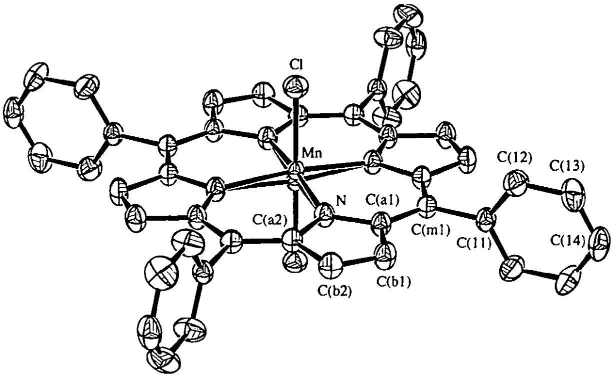


Fig. 1. *ORTEP* diagram of [Mn(TPP)Cl] showing the labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. Porphyrin H atoms are omitted for clarity.

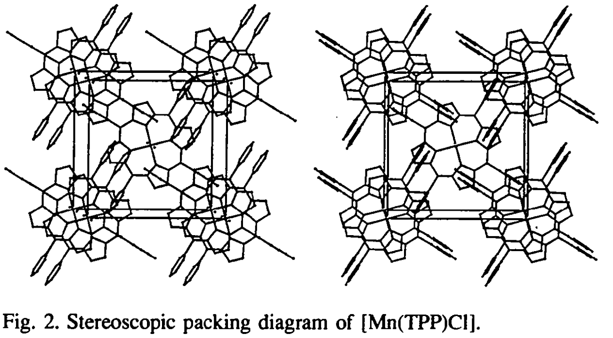


Fig. 2. Stereoscopic packing diagram of [Mn(TPP)Cl].

Experimental

This new crystal form with required $4/m$ symmetry for the title compound was obtained in the course of our synthetic work on μ-oxo- and μ-hydroxomanganese(III) tetraphenylporphyrinate complexes, and recrystallized from toluene and hexanes.

Crystal data

[Mn($C_{44}H_{28}N_4$)Cl]
$M_r = 703.09$
Tetragonal
$I4/m$
$a = 13.463\ (3)$ Å
$c = 9.864\ (4)$ Å
$V = 1787.9\ (9)$ Å^3
$Z = 2$
$D_x = 1.306$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 246 reflections
$\theta = 5.1–20.8°$
$\mu = 0.481$ mm^{-1}
$T = 293\ (2)$ K
Rectangular prism
0.35 × 0.25 × 0.10 mm
Black

Data collection

Enraf–Nonius FAST area-detector diffractometer
Ellipsoid-mask fitting
Absorption correction: none
4391 measured reflections
946 independent reflections

771 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.0603$
$\theta_{\text{max}} = 26.62°$
$h = -15 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -12 \rightarrow 7$

Refinement

Refinement on F^2
$R(F) = 0.0546$
$wR(F^2) = 0.1293$
$S = 1.084$
946 reflections
73 parameters
H atoms idealized, riding (C—H 0.93 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 2.7218P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.306$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.348$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn	0	0	0.0158 (15)	0.034 (2)
Cl	0	0	0.2486 (3)	0.0551 (8)
N	−0.0379 (2)	0.1433 (2)	0	0.0435 (8)
C(*a*1)	0.0249 (3)	0.2240 (3)	0	0.0443 (9)
C(*a*2)	−0.1329 (3)	0.1822 (3)	0	0.0429 (9)
C(*b*1)	−0.0316 (3)	0.3134 (3)	0	0.0546 (11)
C(*b*2)	−0.1273 (3)	0.2882 (3)	0	0.0526 (11)
C(*m*1)	0.1279 (3)	0.2203 (3)	0	0.0431 (9)
C(11)	0.1841 (3)	0.3155 (3)	0	0.0434 (9)
C(12)	0.2109 (3)	0.3602 (3)	−0.1190 (4)	0.0673 (10)
C(13)	0.2655 (3)	0.4474 (3)	−0.1179 (5)	0.0786 (12)
C(14)	0.2935 (3)	0.4898 (3)	0	0.0694 (15)

Table 2. *Selected geometric parameters (Å, °)*

Mn—Mn$^{\text{i}}$	0.31 (3)	C(*a*2)—C(*m*1$^{\text{ii}}$)	1.385 (5)
Mn—N	2.002 (3)	C(*a*2)—C(*b*2)	1.429 (5)
Mn—Cl	2.297 (15)	C(*b*1)—C(*b*2)	1.332 (6)
Mn—Cl$^{\text{i}}$	2.609 (15)	C(*m*1)—C(11)	1.488 (5)
N—C(*a*1)	1.377 (5)	C(11)—C(12)	1.368 (4)
N—C(*a*2)	1.381 (5)	C(12)—C(13)	1.384 (5)
C(*a*1)—C(*m*1)	1.387 (5)	C(13)—C(14)	1.350 (5)
C(*a*1)—C(*b*1)	1.424 (5)		
Mn$^{\text{i}}$—Mn—N	85.5 (4)	N—C(*a*2)—C(*b*2)	109.2 (3)
N$^{\text{ii}}$—Mn—N	89.65 (6)	C(*m*1$^{\text{ii}}$)—C(*a*2)—C(*b*2)	124.9 (4)
N$^{\text{i}}$—Mn—N	171.1 (8)	C(*b*2)—C(*b*1)—C(*a*1)	107.6 (3)
N—Mn—Cl	94.5 (4)	C(*b*1)—C(*b*2)—C(*a*2)	107.8 (3)
C(*a*1)—N—C(*a*2)	105.7 (3)	C(a2$^{\text{iii}}$)—C(*m*1)—C(*a*1)	123.9 (3)
C(*a*1)—N—Mn	127.1 (2)	C(*a*1)—C(*m*1)—C(11)	118.5 (3)
C(*a*2)—N—Mn	126.9 (2)	C(a2$^{\text{iii}}$)—C(*m*1)—C(11)	117.6 (3)
Mn—N—Mn$^{\text{i}}$	8.9 (8)	C(12$^{\text{iv}}$)—C(11)—C(12)	118.2 (4)
N—C(*a*1)—C(*m*1)	125.9 (3)	C(12)—C(11)—C(*m*1)	120.9 (2)
N—C(*a*1)—C(*b*1)	109.7 (3)	C(11)—C(12)—C(13)	120.5 (3)
C(*m*1)—C(*a*1)—C(*b*1)	124.4 (4)	C(14)—C(13)—C(12)	120.9 (4)
N—C(*a*2)—C(*m*1$^{\text{ii}}$)	125.9 (3)	C(13)—C(14)—C(13$^{\text{iv}}$)	119.0 (4)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-y, x, z$; (iii) $y, -x, -z$; (iv) $x, y, -z$.

Cell determination and intensity data collection were performed on an Enraf–Nonius FAST area-detector diffractometer with an Mo rotating-anode source. Our detailed methods and procedures for small-molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). The centrosymmetric space group $I4/m$ was chosen based on the E statistics and consequently proved by the successful refinement.

Data collection: *MADNES* (Messerschmitt & Pflugrath, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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