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

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Cd	0.24399 (4)	0.2755	0.48899 (7)	1.83 (2)
Cl1	0.3733 (1)	0.0347 (5)	0.5409 (3)	2.17 (5)
Cl2	0.1283 (2)	0.0117 (4)	0.3200 (3)	2.60 (6)
O1	0.2177 (5)	0.3773 (9)	0.1974 (9)	2.3 (2)
O2	0.2392 (6)	0.176 (1)	0.7653 (9)	2.5 (2)
N	0.3836 (6)	−0.096 (1)	1.165 (1)	2.2 (2)
C1	0.2804 (5)	0.036 (1)	0.861 (1)	1.8 (2)
C2	0.3350 (6)	0.073 (1)	1.075 (1)	2.0 (2)
C3	0.4028 (8)	0.234 (1)	1.113 (2)	3.2 (3)

Table 2. *Geometric parameters* (Å, °)

Cd—Cl1	2.621 (3)	C1—O2	1.27 (1)
Cd—Cl1	2.614 (3)	C1—C2	1.56 (1)
Cd—Cl2	2.603 (3)	C2—N	1.47 (1)
Cd—Cl2	2.600 (3)	C2—C3	1.54 (1)
Cd—O1	2.295 (6)	O1—O2	2.26 (1)
Cd—O2	2.357 (7)	Cl1—Cl2	3.566 (3)
C1—O1	1.25 (1)	Cl1—Cl2	3.646 (3)
Cl1—Cd—Cl2	86.1 (1)	Cl2—Cd—O2	90.2 (2)
Cl1—Cd—Cl2	88.57 (7)	O1—Cd—O2	168.7 (3)
Cl1—Cd—Cl2	98.96 (7)	O1—C1—O2	127.6 (7)
Cl1—Cd—Cl2	86.3 (1)	O1—C1—C2	118.2 (7)
Cl1—Cd—O1	98.6 (2)	O2—C1—C2	114.2 (7)
Cl1—Cd—O1	82.9 (2)	C1—C2—C3	110.9 (7)
Cl1—Cd—O2	90.3 (2)	N—C2—C1	108.0 (7)
Cl1—Cd—O2	88.9 (2)	N—C2—C3	111.0 (8)
Cl2—Cd—O1	97.0 (2)	Cd—Cl1—Cd	88.15 (6)
Cl2—Cd—O1	86.9 (2)	Cd—Cl2—Cd	88.83 (7)
Cl2—Cd—O2	86.7 (2)		

In the refinement, $\Sigma w(|F_o|-|F_c|)^2$ was minimized. The weighting scheme used was $w=1/\sigma^2(F_o^2)$ in which $\sigma(F_o^2) = [C+1/4(t_c/t_b)\times(b_1+b_2) + (pI)^2]^{1/2}$ where C is the total number of counts per peak, t_c is the time spent counting peak density, t_b is the time spent counting one side of background, b_1 is the high-angle background count, b_2 is the low-angle background count, p is the fudge factor and $I = C-1/2(t_c/t_b)(b_1 + b_2)$.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55793 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1025]

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Structure of Monomeric Hydrated Manganese(III) Tetra(4-*N*-methylpyridyl)porphyrin Pentachloride

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Abstract

The structure of the title compound, diaqua{2,7,12,17-tetrakis(1-methyl-4-pyridyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1(21),2,4,6-(22),7,9,11(23),12,14,16(24),17,19-dodecaene-N^{21},N^{22},N^{23},N^{24}}manganese(III) pentachloride heptahydrate, Mn-tmpyp, is the second example of a planar diaqua-ligated metalloporphyrin with an extensive anion–water network which interdigitates between successive layers of porphyrins. The Mn atoms have near octahedral geometry: Mn—N1 2.012 (5), Mn—N2 2.013 (5), Mn—O1 2.221 (5) Å, N1—Mn—O1 90.2 (2), N2—Mn—O1 89.1 (2)°. The pyridyl planes are inclined by 65.0° (C11–C12–C13–N12–C14–C15) and 71.2° (C16–C17–C18–N11–C19–C20) with respect to the least-squares plane through the porphyrin.

Comment

The reactions of iron(III) and manganese(III) tetraarylporphyrins have been extensively employed to model the chemistry of haem enzymes and to develop new oxidation catalysts (Meunier, 1986; Mansuy, 1987; Mansuy, Battioni & Battioni, 1989). The [Mn^{III}(tmpyp)]$^{5+}$ structure is isomorphous with

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that of $[Fe^{III}(tmpyp)]^{5+}$ (Körber, Lindsay Smith, Prince, Rizkallah, Reynolds & Shawcross, 1991). The exchange of the central cation has no effect on the nature and organization of the axial ligands or on the extensive chloride–water network uniquely found in these two structures of charged monomeric metalloporphyrins. The structure of the octaperchlorate of the μ-oxo dimer of $[Fe^{III}(tmpyp)]$ (Ivanca, Lappin & Scheidt, 1991) is organized completely differently.

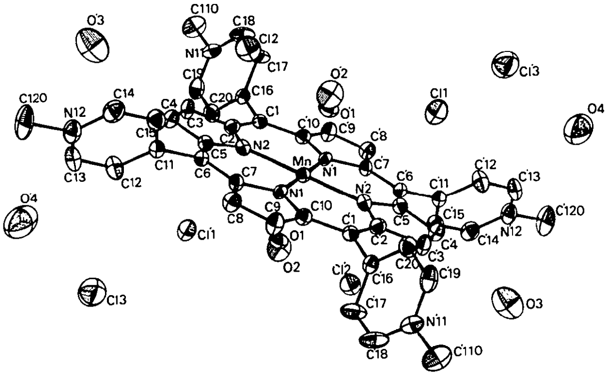

Fig. 1. *ORTEP*II plot of a whole molecule of Mn^{III}(tmpyp) with the Cl counterions and water molecule O atoms. Thermal parameters are depicted as 38% probability ellipsoids. Symmetry-related atoms are denoted by primes.

Experimental

Crystal data

$[Mn(C_{44}H_{36}N_8)(H_2O)_2]Cl_5.7H_2O$
M_r = 1071.2
Monoclinic
$P2_1/c$
a = 13.630 (6) Å
b = 11.775 (2) Å
c = 16.316 (8) Å
β = 108.26 (3)°
V = 2486.7 (18) Å^3
Z = 2
D_x = 1.43 (1) Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 250 reflections
θ = 4.5–26°
μ = 0.538 mm^{-1}
T = 295 K
Plate
0.6 × 0.5 × 0.03 mm
Greenish brown
Crystal source: material from NenTech Ltd; recrystallized from H_2O/acetone

Data collection

Enraf-Nonius FAST diffractometer
On-line box-integration data collection
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.699, T_{max} = 1.211
10116 measured reflections
4215 independent reflections

4215 observed reflections [criterion for observation not applicable for FAST data collection]
R_{int} = 0.105
θ_{max} = 26°
$h = -16 \rightarrow 15$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 19$
Standard reflections not applicable for FAST data collection

Refinement

Refinement on F
Final R = 0.047
wR = 0.053
2088 reflections
305 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.051

$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: Enraf-Nonius FAST software *MADNES* (Pflugrath & Messerschmidt, 1986). Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

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

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

	x	y	z	U_{eq}
Mn	0.5000	0.0000	0.0000	0.025 (1)
N1	0.4291 (3)	0.1360 (4)	−0.0676 (3)	0.028 (3)
N2	0.3618 (3)	−0.0727 (4)	−0.0154 (3)	0.027 (3)
C1	0.5804 (4)	0.2546 (5)	−0.0589 (4)	0.029 (4)
C2	0.4755 (5)	0.2343 (5)	−0.0844 (4)	0.030 (4)
C3	0.3982 (5)	0.3138 (6)	−0.1299 (4)	0.036 (4)
C4	0.3051 (5)	0.2647 (5)	−0.1398 (4)	0.035 (4)
C5	0.3244 (4)	0.1545 (5)	−0.1011 (4)	0.029 (4)
C6	0.2465 (4)	0.0789 (5)	−0.0950 (4)	0.028 (4)
C7	0.2648 (4)	−0.0274 (5)	−0.0567 (4)	0.028 (4)
C8	0.1858 (5)	−0.1073 (6)	−0.0553 (4)	0.038 (4)
C9	0.2350 (5)	−0.2007 (6)	−0.0121 (4)	0.038 (4)
C10	0.3424 (4)	−0.1790 (5)	0.0115 (4)	0.030 (4)
C11	0.1377 (4)	0.1149 (5)	−0.1319 (4)	0.030 (4)
C12	0.0918 (5)	0.1333 (6)	−0.2195 (4)	0.046 (5)
C13	−0.0087 (5)	0.1657 (7)	−0.2509 (5)	0.048 (5)
C14	−0.0243 (5)	0.1609 (6)	−0.1130 (5)	0.046 (5)
C15	0.0759 (5)	0.1303 (6)	−0.0787 (4)	0.040 (4)
C16	0.6155 (4)	0.3677 (5)	−0.0793 (4)	0.029 (4)
C17	0.6568 (6)	0.4466 (6)	−0.0150 (5)	0.051 (5)
C18	0.6873 (6)	0.5510 (6)	−0.0348 (5)	0.058 (6)
C19	0.6368 (5)	0.5036 (6)	−0.1803 (4)	0.042 (4)
C20	0.6077 (5)	0.3971 (6)	−0.1626 (4)	0.039 (4)
N11	0.6750 (4)	0.5787 (5)	−0.1171 (4)	0.040 (4)
N12	−0.0662 (4)	0.1784 (5)	−0.1984 (4)	0.042 (4)
C110	0.7015 (7)	0.6942 (6)	−0.1372 (6)	0.066 (6)
C120	−0.1783 (5)	0.2096 (8)	−0.2354 (6)	0.073 (7)
O1	0.5039 (3)	−0.0830 (4)	−0.1212 (3)	0.041 (3)
O2	0.6542 (4)	−0.0129 (5)	−0.1842 (3)	0.072 (4)
O3	0.1152 (5)	0.0569 (6)	0.3494 (5)	0.114 (6)
O4	−0.0152 (8)	0.6689 (8)	0.9413 (5)	0.155 (9)
Cl1	0.4318 (2)	−0.1687 (2)	0.3344 (2)	0.054 (1)
Cl2	0.1122 (2)	0.1048 (2)	0.1528 (1)	0.058 (1)
Cl3	0.0990 (3)	−0.0598 (3)	−0.3953 (3)	0.097 (3)

The crystals were highly mosaic (mosaicity 1.6°) but diffracted to 0.8 Å resolution. The FAST data collection was performed with one standard setting and two cross-orientations. The structure was solved by direct methods. Weak reflections with $|F| < 2\sigma(F)$ were rejected at the refinement stage. H atoms were held fixed at calculated positions. Their temperature factors were refined in two groups, one for the methyl H atoms and one for the H atoms of the remainder of the structure. Attempts to refine the atomic positions and thermal parameters of the H atoms individually resulted in divergence of the refinement. H atoms of the water molecules were not modelled. Atoms C13 and O5 alternately occupy the same position. This disorder was modelled by assigning an occupancy factor of 0.75 to C13.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55862 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE1001]

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Structure of (2,4-Pentanedionato-*O*,*O'*)-bis(phenyl 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-diyl phosphite-*P*)rhodium

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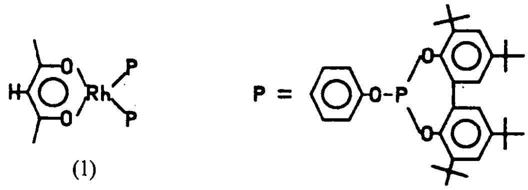
Abstract

The crystal structure of the title compound has been determined. The square-planar coordination of the complex is tetrahedrally distorted. The two phosphite ligands of the Rh complex are deformed as a result of steric interactions.

Comment

The hydroformylation of otherwise unreactive internal and branched alkenes can be achieved by using bulky phosphite-modified Rh catalysts (van Leeuwen & Roobeek, 1983; Tokitoh & Yoshimura, 1987, 1989; Billig, Abatjoglou, Bryant, Murray & Maher, 1988; Polo, Real, Claver, Castillon & Bayon, 1990; Tręciak & Ziolkowski, 1988). The title compound (1) is a precursor of one of these catalysts, and therefore the steric conformation of this bisphosphite Rh complex is of use in the study of the catalytic cycle of these catalysts. The triphenylphosphite analogue (2) of the title compound has been crystallized by Leipoldt, Lamprecht & van Zyl (1985). Other bulky phosphites, *i.e.* tri(2-*tert*-butylphenyl) phosphite (3) (Jongsma, Challa & van Leeuwen, 1991), tri(2,4,6-trimethylphenyl) phosphite (4) (J. Jongsma, G. Challa & P. W. N. M. van Leeuwen, unpublished results) and bi(2-*tert*-butyl-6-methylphenyl) phenyl phosphite (5) (Jongsma, Kimkes, Challa & van Leeuwen, 1992), exclusively yielded the monophosphite Rh complex Rh(acac)(CO)*P* (acac = 2,4-pentanedionato, CO = carbonyl and *P* = phosphite ligand).



(1)

The identification of the atoms and the configuration are shown in the *PLUTO* drawing of Fig. 1. Each asymmetric unit contains one complete molecule of the title compound with no atom sitting at a special position and two half molecules of disordered toluene solvent molecules. The triclinic unit cell contains two discrete molecules of the title compound and two toluene molecules separated by normal van der Waals distances (Bondi, 1964). Both toluene molecules possess a crystallographically imposed centre of inversion. The square-planar structure of the complex (1) is tetrahedrally distorted [distances of atoms from root-mean-square (r.m.s.) plane of P1-P2-O2-O1: P1 −0.096 (7), P2 0.096 (6), O1 0.108 (7), O2 −0.110 (6) Å]. The central Rh atom is in the plane [distance from r.m.s. plane: Rh 0.004 (6) Å]. Steric hindrance of the two phosphite groups is demonstrated by the large P1—Rh—P2 angle of 99.87 (3)°, *versus* 94.8 (2)° for the triphenyl phosphite Rh complex (2) (Leipoldt, Lamprecht & van Zyl, 1985). The O1—Rh—O2 angle [89.41 (2)°] is only slightly larger than that of the triphenyl phosphite analogue (2) [88.8 (2)°]. The

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