

The first phosphite complex of a metalloporphyrin

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Received 27 January 2003

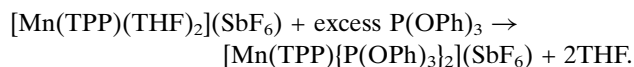
Accepted 25 February 2003

Online 21 March 2003

(Diphenyl phosphite- κO)(5,10,15,20-tetraphenylporphyrinato- $\kappa^4 N$)manganese(III) hexafluoroantimonate(V), $[\text{Mn}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{C}_{12}\text{H}_{11}\text{O}_3\text{P})](\text{SbF}_6)$, is the first example of a structurally characterized diaryl or dialkyl phosphite complex of a metalloporphyrin ion. The axial phosphite ligand binds to the Mn^{III} ion *via* the $\text{P}=\text{O}$ O atom, affording a nominally five-coordinate complex with an $\text{Mn}-\text{O}$ distance of 2.120 (4) Å. The mean porphyrin $\text{Mn}-\text{N}$ distance is 2.000 (4) Å and the Mn^{III} ion is displaced from the 24-atom porphyrin mean plane by 0.1548 (13) Å towards the axial O atom. The porphyrin adopts a marked saddle conformation, with a small domed component. The saddle distortion of the porphyrin ligand reflects the tight back-to-back dimers formed in the lattice by pairs of neighboring cations. The 'non-covalent' dimers in the lattice exhibit an unusual (weak) η^2 -type coordination of a pyrrole $\text{C}=\text{C}$ bond from a neighboring molecule, with $\text{Mn}^{\text{III}} \cdots \text{C}$ distances of 3.697 (5) and 3.537 (5) Å.

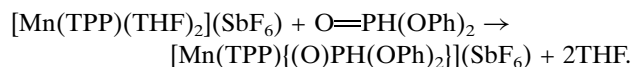
Comment

During the course of our work on the synthesis and characterization of novel complexes of metalloporphyrins (Munro *et al.*, 1999, 2001), we isolated crystals of a novel Mn^{III} -porphyrin complex, (I), from a reaction intended to produce the bis(triphenyl phosphite) derivative $[\text{Mn}(\text{TPP})\{\text{P}(\text{OPh})_3\}_2](\text{SbF}_6)$ (where TPP is 5,10,15,20-tetraphenylporphyrinate and THF is tetrahydrofuran):

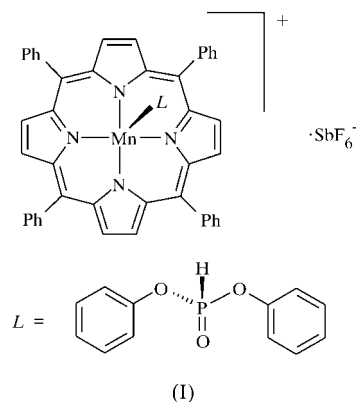


Since we were unable to cleanly isolate the desired reaction product, which had a ^{31}P NMR signal at 116.91 p.p.m. in CDCl_3 solution, and instead obtained crystals of the diphenyl phosphite derivative, we analyzed the commercial source of triphenyl phosphite by GC-MS and found that it contained *ca* 1% diphenyl phosphite. Evidently, this contaminant in the

commercial reagent was present in a sufficiently large quantity under the reaction conditions to react with the Mn^{III} -porphyrin according to:



This unexpected behavior in the presence of a large excess of triphenyl phosphite clearly reflects the oxophilic nature of Mn^{III} (Scheidt, 2000) and the fact that diphenyl phosphite is sterically less hindered than triphenyl phosphite and thus, we presume, a ligand with an intrinsically higher affinity constant for a metalloporphyrin.



The room-temperature X-ray crystal structure of (I) is shown in Fig. 1. The P-bound phosphite H atom (H71) is located in a difference Fourier map and was refined isotropically. There is a well defined, though relatively weak, hydrogen bond [2.64 (5) Å] between this H atom and an F atom (F2) of the SbF_6^- counter-ion; the $\text{P}-\text{H}71 \cdots \text{F}2$ angle is 167 (3)°. As discussed below, the porphyrin conformation is clearly non-planar (saddle distortion) and the Mn^{III} ion is located 0.1548 (13) Å above the 24-atom porphyrin mean plane (Fig. 2) to give a nominally square-pyramidal coordination geometry. The $\text{Mn}-\text{O}1$ distance is 2.120 (4) Å and the mean porphyrin $\text{Mn}-\text{N}$ distance is 2.000 (4) Å. The *trans* $\text{N}-\text{Mn}-\text{N}$ angles average 170.0 (3)° (Table 1), a value which is consistent with the square-pyramidal coordination geometry of the metal ion. The coordination group is, on the whole, similar in structure to that reported for $[\text{Mn}(\text{TPP})(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)$ (Williamson & Hill, 1986), in which the $\text{Mn}-\text{O}$ and porphyrin $\text{Mn}-\text{N}$ distances are 2.105 (4) and 1.995 (7) Å, respectively, and the metal ion displacement is 0.17 Å.

The porphyrin core geometry and averaged chemically unique distances and angles of (I) are shown in Fig. 2. As noted above, the porphyrin conformation is predominantly of the saddle type (Scheidt & Lee, 1987). However, the out-of-plane location of the Mn^{III} ion results in an admixture of a classical saddle conformation (pairs of pyrrole β -C atoms alternately displaced above and below the porphyrin mean plane) and a domed conformation that commonly results from five-coordination in metalloporphyrins (Scheidt, 2000). The maximum out-of-plane displacement is shown by the pyrrole

β -C atom C202 [0.400 (6) Å]. The mean absolute perpendicular displacements of the porphyrin N, α -, β -, and *meso*-C atoms are 0.03 (3), 0.13 (4), 0.35 (4), and 0.07 (5) Å, respectively.

The saddle distortion of the porphyrin macrocycle reflects the conformational adjustments that are required to accommodate the canted *meso*-phenyl groups (Munro *et al.*, 1992), which are clearly tipped towards the plane of the pyrrole rings. More specifically, the dihedral angles between the planes of the four *meso*-phenyl groups and the 24-atom porphyrin mean

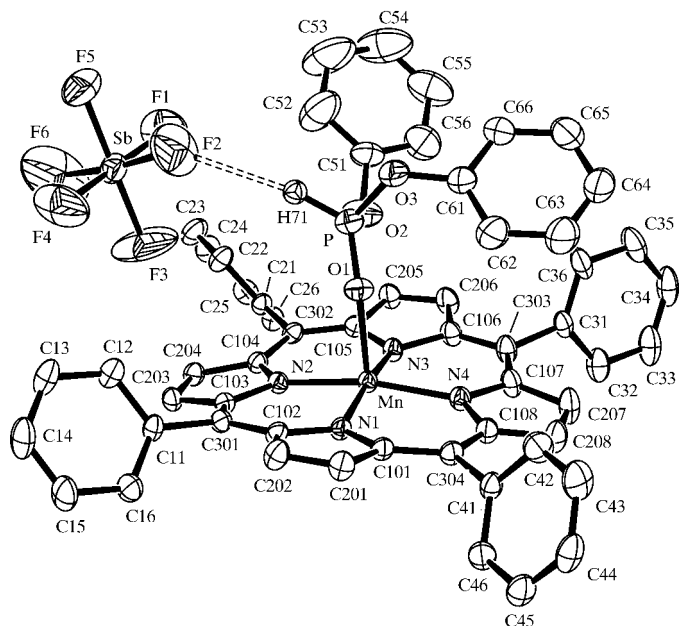


Figure 1
Labeled ORTEP-3 (Farrugia, 1997) view of (I) (30% probability displacement ellipsoids), showing the hydrogen bond between atoms F2 and H71 (all other H atoms have been omitted for clarity) and the overall molecular conformation. Only the major disordered component is shown.

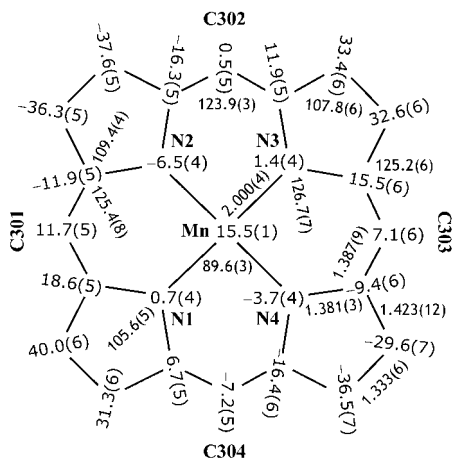


Figure 2
Formal diagram of (I), showing the perpendicular displacements (in units of 0.01 Å) of each atom from the 24-atom porphyrin mean plane, as well as the average structural parameters for each chemically unique class of bond and angle in the porphyrin macrocycle.

plane are 53.72 (13)° (C11–C16, phenyl group attached to C301), 55.14 (15)° (C21–C26, phenyl attached to C302), 82.2 (4)° (C31–C36, phenyl attached to C303), and 59.96 (19)° (C41–C46, phenyl attached to C304), respectively. These acute dihedral angles are consistent with the fact that the porphyrin

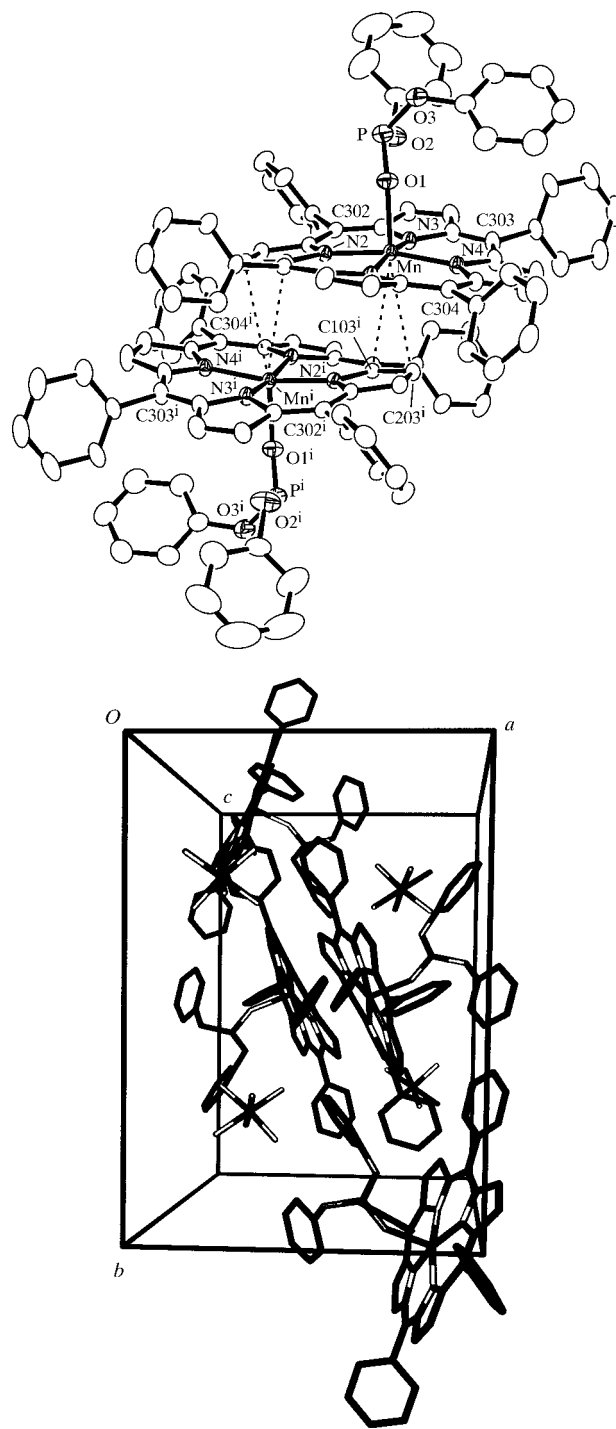


Figure 3
Selectively labeled view (top) of (I) (30% probability displacement ellipsoids), showing a symmetry-related cation pair [symmetry code: (i) $1 - x, 1 - y, 1 - z$] and two of the significant short contacts between the dimer units. A perspective view of the unit cell of (I) (bottom) illustrates the interaction in relation to the remaining unit-cell contents. H atoms have been omitted for clarity.

cations pack as rather tight (formally non-covalent) dimers in a back-to-back fashion and that rotation of the *meso*-phenyl groups facilitates the close approach of the two porphyrin rings. This is illustrated in Fig. 3, which shows that the constituents of each dimer are related by a center of inversion between the pair of cations.

The canted phenyl groups appended to porphyrin *meso*-C atoms C301 and C302 apparently push the pyrrole ring containing atom N2 below the porphyrin mean plane. However, there are actually two interesting types of interaction that directly or indirectly involve this particular pyrrole ring. The first is steric strain (van der Waals repulsion) with respect to the *meso*-phenyl groups appended to C301 and C302, as noted above. One consequence of these interactions is that a 'pocket' is created that partially accommodates the SbF_6^- ion. Moreover, in addition to the $\text{H71} \cdots \text{F2}$ hydrogen bond, several other moderate-to-weak hydrogen bonds involving the F atoms evidently stabilize the location of the anion at this site. These include $\text{H52} \cdots \text{F1}$ (2.57 Å; $\text{C52} - \text{H52} \cdots \text{F1} = 147^\circ$), $\text{H42}^i \cdots \text{F2}$ (2.67 Å; $\text{C42}^i - \text{H42}^i \cdots \text{F2} = 136^\circ$), $\text{H22} \cdots \text{F3}$ (2.53 Å; $\text{C22} - \text{H22} \cdots \text{F3} = 155^\circ$), $\text{H25}^{ii} \cdots \text{F4}$ (2.60 Å; $\text{C25}^{ii} - \text{H25}^{ii} \cdots \text{F4} = 142^\circ$), and $\text{H26}^{ii} \cdots \text{F5}$ (2.58 Å; $\text{C26}^{ii} - \text{H26}^{ii} \cdots \text{F5} = 146^\circ$) [symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$]. We surmise that these interactions may collectively dictate the orientation of the axial diphenyl phosphite ligand, which exhibits $\text{N3} - \text{Mn} - \text{O1} - \text{P}$ and $\text{Mn} - \text{O1} - \text{P} - \text{H71}$ torsion angles of 22.2 (5) and 93 (2)°, respectively. The $\text{H22} \cdots \text{F3}$ hydrogen bond probably also accounts, at least in part, for the orientation of the phenyl group appended to C302.

The second type of interaction with the N2 pyrrole ring involves the Mn^{III} ion of a neighboring cation. In fact, compound (I) is best regarded as being pseudo-six-coordinate, since the Mn^{III} ion of one cation makes two short contacts with a pair of C atoms in a neighboring cation, with $\text{Mn} \cdots \text{C103}^{\text{iii}}$ and $\text{Mn} \cdots \text{C203}^{\text{iii}}$ [symmetry code: (iii) $1 - x, 1 - y, 1 - z$] distances of 3.697 (5) and 3.537 (5) Å, respectively. These contact distances are considerably shorter than the sum of the van der Waals radii of the Mn and C atoms concerned (3.86 Å). Given that C103 and C203 formally belong to a pyrrole $\text{C}=\text{C}$ bond, it is not unreasonable to suggest that there is a weakly coordinated alkene-like ligand (η^2 -binding mode) occupying the sixth coordination site in (I). Finally, we conclude that it is perhaps the latter interaction that best explains the dimeric structure of (I) in the solid state and thus both the canted *meso*-phenyl groups and the resulting saddle conformation of the porphyrin ring.

Experimental

General experimental methods were as described previously (Munro *et al.*, 2001). Triphenyl phosphite (Aldrich) was stored under nitrogen but no further steps to purify the commercial reagent were undertaken. H_2TPP (5,10,15,20-tetraphenylporphyrin) was synthesized according to published procedures (Barnett *et al.*, 1975). $[\text{Mn}(\text{TPP})\text{Cl}]$ was prepared according to the method of Adler *et al.* (1970). To $[\text{Mn}(\text{TPP})\text{Cl}]$ (150 mg, 0.21 mmol) and AgSbF_6 (88 mg, 0.26 mmol;

Aldrich) in a 250 ml Schlenk tube under nitrogen was added freshly distilled tetrahydrofuran (50 ml, THF). The solution was stirred for *ca* 12 h at room temperature. The THF was then removed *in vacuo* and the green-brown solid obtained redissolved in dichloromethane (50 ml). The solution was filtered into a 250 ml Schlenk tube containing triphenyl phosphite (1.1 ml, 4.3 mmol) and the resulting solution left to stir at room temperature for 10 min. The red-brown solution was then transferred into 12 Schlenk tubes in *ca* 4 ml aliquots and layered with hexane. X-ray quality crystals were observed after 4 d. The yield was not calculated as the bulk material was not pure. No further analysis beyond an X-ray structure determination was attempted.

Crystal data

$[\text{Mn}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{C}_{12}\text{H}_{11}\text{O}_3\text{P})](\text{SbF}_6)$	$D_x = 1.525 \text{ Mg m}^{-3}$
$M_r = 1137.57$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 13.719$ (2) Å	$\theta = 2-12^\circ$
$b = 20.817$ (3) Å	$\mu = 0.91 \text{ mm}^{-1}$
$c = 17.390$ (2) Å	$T = 296$ (2) K
$\beta = 94.132$ (11)°	Cube, purple-black
$V = 4953.7$ (12) Å ³	$0.5 \times 0.5 \times 0.5 \text{ mm}$
$Z = 4$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 25.0^\circ$
ω -2 θ scans	$h = -1 \rightarrow 16$
10 668 measured reflections	$k = -1 \rightarrow 24$
8694 independent reflections	$l = -20 \rightarrow 20$
6205 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.017$	frequency: 120 min
	intensity decay: 4%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1251P)^2 + 2.2623P]$
$R(F) = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.202$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.98 \text{ e \AA}^{-3}$
8694 reflections	$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$
660 parameters	
H atoms treated by a mixture of independent and constrained refinement	

The phosphite H atom (H71) was located by a difference Fourier synthesis calculation and was refined isotropically without restraints. All other H atoms were calculated using the standard riding model of *SHELXL97* (HFIX 43 instruction; Sheldrick, 1997), with $\text{C}-\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The C31–C36 phenyl ring was disordered about two positions that were consistent with an in-plane (up-down) translational or wagging motion. The unique ring positions were modeled using rigid group constraints ($\text{C}-\text{C}$ distances fixed at 1.39 Å and ring atoms constrained to lie within 0.1 Å of the same plane). Rigid bond restraints, in which the components of the anisotropic displacement parameters in the direction of each bond were restrained to be equal within an effective s.u. of 0.01 \AA^2 , were also applied. The anisotropic displacement parameters of the C atoms comprising each ring were further restrained with an effective s.u. of 0.03 \AA^2 , so that their U_{ij} components approximated to isotropic behavior (the isotropic U values were free to vary). The site-occupancy factor for the minor component of the disordered phenyl ring converged to a value of 0.33 (4). The anisotropic displacement parameters for atoms C52–C54 are suggestive of rotational motion for the phenyl group attached to O2. However, attempts to fit two

Table 1

Selected geometric parameters (Å, °).

Mn—N1	1.995 (4)	P—O1	1.443 (4)
Mn—N3	2.000 (4)	P—O2	1.535 (6)
Mn—N2	2.003 (4)	P—O3	1.560 (5)
Mn—N4	2.003 (4)	O2—C51	1.451 (6)
Mn—O1	2.120 (4)	O3—C61	1.390 (6)
N1—Mn—N3	171.69 (18)	N2—Mn—O1	93.41 (17)
N1—Mn—N2	89.60 (16)	N4—Mn—O1	98.38 (18)
N3—Mn—N2	89.20 (16)	O1—P—O2	106.3 (3)
N1—Mn—N4	89.75 (16)	O1—P—O3	115.4 (3)
N3—Mn—N4	89.75 (17)	O2—P—O3	109.2 (3)
N2—Mn—N4	168.21 (18)	P—O1—Mn	146.7 (3)
N1—Mn—O1	92.51 (17)	C51—O2—P	124.6 (5)
N3—Mn—O1	95.76 (17)	C61—O3—P	123.0 (4)
O1—Mn—N1—C101	−86.7 (4)	O3—P—O2—C51	−44.9 (7)
O1—Mn—N1—C102	74.6 (4)	O1—P—O3—C61	51.4 (6)
O1—Mn—N2—C103	−86.4 (4)	O2—P—O3—C61	−68.2 (6)
O1—Mn—N2—C104	92.0 (4)	C102—C301—C11—C16	−60.6 (7)
O1—Mn—N3—C106	82.8 (5)	C103—C301—C11—C12	−60.0 (7)
O1—Mn—N3—C105	−78.5 (4)	C105—C302—C21—C26	62.7 (7)
O1—Mn—N4—C107	−90.5 (5)	C104—C302—C21—C22	59.3 (7)
O1—Mn—N4—C108	90.8 (5)	C107—C303—C31—C32	78.6 (9)
O2—P—O1—Mn	−15.3 (6)	C106—C303—C31—C36	74.2 (9)
O3—P—O1—Mn	−136.5 (5)	C108—C304—C41—C42	64.4 (8)
N1—Mn—O1—P	−157.2 (5)	C101—C304—C41—C46	65.7 (7)
N3—Mn—O1—P	22.1 (5)	P—O2—C51—C52	−59.8 (8)
N2—Mn—O1—P	−67.4 (5)	P—O2—C51—C56	118.5 (6)
N4—Mn—O1—P	112.7 (5)	P—O3—C61—C62	−67.3 (7)
O1—P—O2—C51	−170.0 (6)	P—O3—C61—C66	117.3 (5)

ring positions for this group using standard rigid-group constraints (*SHELXL97* AFIX 66 instruction) were not successful since the O2—C51—C52 angle became chemically unfeasible (94.6°) for one of the rings. Furthermore, attempts to restrain this angle to 120° lead to an unstable refinement. The C51—C56 phenyl ring was therefore modeled as a single rigid group with the same restraints as applied to the disordered phenyl rings appended to C303. Lastly, a rigid group

refinement for the phenyl ring attached to O3 (C61—C66) was used to prevent the C—C bonds from becoming unreasonably short.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank the University of Natal Research Fund and the National Research Foundation (Pretoria) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1160). Services for accessing these data are described at the back of the journal.

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