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METAL COMPLEXES WITH TETRAPYRROLE LIGANDS

XV *. A CARBONYLOSMIUM PORPHODIMETHENE: SYNTHESIS, AND DETERMINATION OF THE CRYSTAL AND MOLECULAR STRUCTURE

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Summary

A novel osmium porphodimethene, carbonyl (α,γ-dimethyl-α,γ-dihydrooctaethylporphinato)pyridineosmium(II) [Os(OEPMe$_2$)CO · Py], has been prepared by reductive methylation of carbonyl(octaethylporphinato)pyridineosmium(II) [Os(OEP)CO · Py]. The constitution has been determined by elemental analysis, electronic absorption-, IR, NMR, and mass spectra. The *syn*-axial configuration of the two methyl and the carbonyl groups follows from an analysis of X-ray diffraction data collected with a Syntex P1 diffractometer. The compound crystallizes in an orthorhombic four-molecule unit cell (space group *Pnma*). The more important structural parameters have the following values: d[Os—N-(OEPMe$_2$)] = 2.067 Å, d[Os—N(Py)] = 2.230 Å, d[Os—C(CO)] = 1.828 Å, and d[C≡O] = 1.15 Å; the porphodimethene ligand shows a roof-like folding defined by an angle of 38.1° between the normals of the essentially planar pyrromethene halves of the macrocycle; the Os atom lies 0.18 Å above the plane of the four N atoms of the (OEPMe$_2$) ligand in the direction of the CO group. The decreased value of the CO stretching frequency in Os(OEPMe$_2$)CO · Py ($\tilde{\nu}$(CO) = 1863 cm^{-1}) compared with that in Os(OEP)CO · Py ($\tilde{\nu}$(CO) = 1902 cm^{-1}) indicates an increased back-bonding to the CO group, and hence, a diminished back-bonding to the porphodimethene ligand.

Introduction

An essential component of the toxic action of carbon monoxide is the formation of carbonyl hemoglobin in which the free coordination site at the heme

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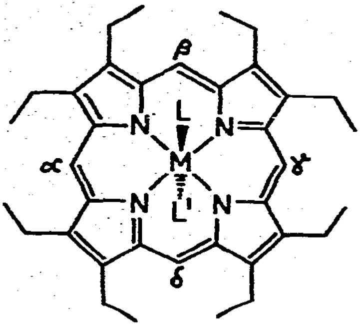
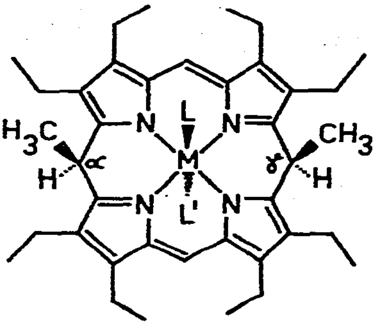
* For part XIV see ref. 5.

iron is blocked by a CO molecule and thus is no longer accessible to the O_2 molecule. Hemes are iron(II)porphyrins, e.g. the rather labile carbonyl(octaethylporphinato)pyridineiron(II) [Ia; Fe(OEP)CO · Py] and are being studied by several research groups. For a recent review see ref. 1. Especially noteworthy in this context is "picket fence heme" [2], the carbonyl-(*N*-methylimidazole)-derivative of which has been isolated [3] and investigated by X-ray diffraction methods [4]. The "picket fence heme" is a sterically and electronically modified heme.





(I) M(OEP)LL′
(Ia) M = Fe, L = CO, L′ = Py
(Ib) M = Os, L = CO, L′ = Py
(Ic) M = Os, L = N_2, L′ = THF

(II) $M(OEPMe_2)LL'$
(IIa) M = Fe, L = CO, L′ = Py
(IIb) M = Os, L = CO, L′ = Py

Another instance of such a modification is provided by the iron porphodimethenes [II; M = Fe; $Fe(OEPMe_2)LL'$] which are formally and chemically closely related to the "octaethylhemes" I (M = Fe) [5]. The carbonyl(porphodimethenato)pyridine heme IIa has been characterized spectrally [6], but not yet isolated as a pure solid because of its extreme sensitivity; therefore, the *syn*-axial configuration of the CO ligand and the methyl groups at C_α and C_γ indicated in the formula IIa is as yet unproven.

The replacement of iron by osmium in the heme Ia gave the very stable osmium porphyrin Os(OEP)CO · Py (Ib) [7]. Generally, the adducts of osmium porphyrins with small molecules are far more stable than the corresponding adducts of hemes, as shown by the successful characterization of $Os(OEP)N_2$ · THF (Ic) [8]. The synthesis of the osmium analogue of IIa, $Os(OEPMe_2)CO$ · Py (IIb), was therefore undertaken in order to obtain a stable material which could be used to establish the configuration of the axial methyl groups and the CO molecule in this kind of porphodimethene complex.

Synthesis and spectral characterization

The synthesis of $Fe(OEPMe_2)CO$ · Py (IIa) involved five different chemical processes and the isolation of two intermediates because the reductive methylation [9] of Fe(OEP) does not work [5]. However, $Os(OEPMe_2)CO$ · Py (IIb) could be obtained in a one-step synthesis by direct reductive methylation of Os(OEP)CO · Py (Ib). On reduction with sodium anthracenide, only a green anionic species was observed; in this respect, the course of the reaction resembled the reductive methylation of Pt(OEP) [10]. The yield (19%) was, however, also low (Pt: 15%). The stability of the product, however, facilitated its isolation which was achieved by repeated silica-gel chromatography and crystallization. Especially noteworthy is the retainment of the pyridine ligand throughout the whole procedure.

Os(OEPMe$_2$)CO · Py (IIb) forms brown, air-stable crystals. The orange-coloured solutions have a single strong absorption band at 439 mm which is hypsochromically shifted relative to its iron analogue, IIa (λ_{max} = 442 nm [6]). A similar hypsochromic shift is observed when Fe is replaced by Os in I, indicating an increased back-bonding from the heavy metal to both the porphyrin and the porphodimethene ligand [1].

However, back-bonding to the tetrapyrrole ligand seems to be less pronounced in the porphodimethene ligand because both the carbonyls IIa and IIb display a lower CO-stretching frequency than the corresponding reference compounds Ia and Ib [Fe(OEPMe$_2$)CO · Py: 1932 cm^{-1} [6]; Fe(OEP)CO · Py: about 1970 cm^{-1} [6]; Os(OEPMe$_2$)CO · Py: 1863 cm^{-1}, Os(OEP)CO · Py: 1902 cm^{-1} [7]]. Obviously, breaking up the macrocyclic π-electron system reduces its π-acceptor capacity; probably the roof-like folding described in the next section works in the same direction. Some π-electron acceptance by the porphodimethene system may also be reflected in the rather low frequency of the "methene band" at 1592 cm^{-1}, which normally occurs at higher values [10] although no systematic shifts of this band have been found so far. The other three strong, typical bands of the porphodimethene core [11] at 1224, 998 and 864 cm^{-1} are also present.

The ^{1}H NMR spectrum of IIb is fully in accord with the structure, although some of the pyridine proton signals are hidden by porphodimethene signals. A multiplet showing its highest peak at 6.9 ppm clearly arises from pyridine protons, its chemical shift showing a much lower shielding than in the related complex Ib where it appears at 5.8 ppm [7]. This indicates the absence of the macrocyclic component of ring current effects. The proton resonances of the porphodimethene core in the metal-free system, H$_2$(OEPMe$_2$), and in nine different metal complexes have been discussed elsewhere [10,11]. Only the signals of the two sets of protons located at the methine bridges, $C_{\alpha,\gamma}$ and $C_{\beta,\delta}$, show significant shifts from the mean values of the ten compounds established in the previous analysis [10]. The increased shielding of the β,δ-protons and the deshielding of the α,γ-protons can perhaps be explained by a ring current effect exerted by the pyridine ligand which resides in the appropriate orientation for the production of such an effect; this is demonstrated in the next section (Fig. 1). The CO ligand has roughly the same influence on the shielding of the methyl protons at $C_{\alpha,\gamma}$ as the axial methoxy group in Al(OEPMe$_2$)OMe or Ga(OEPMe$_2$)OMe [10,11].

The mass spectrum does not show the intact molecular ion; the ion [Os(OEPMe$_2$)CO]$^+$ is the species appearing with the highest mass. The cracking pattern of this ion (listed in the experimental section) is typical for all these porphodimethene complexes [5,9,10]. Probably the pyridine ligand is thermally eliminated prior to ionization. The ion Py$^+$ appears in the low mass region with variable intensity and proves the presence of Py in the molecule.

Determination of the crystal and molecular structure

The numbering system employed in Tables 1—4 for the carbon and nitrogen atoms in the asymmetric structure unit is displayed in Figs. 1 and 2. Figure 1 is a computer-drawn [12] model in perspective of the $Os(OEPMe_2)CO \cdot Py$ molecule as it exists in the crystal. Bond parameters (with estimated standard deviations) * are listed in Tables 3 and 4. The crystallographically imposed mirror plane passes through the atoms O, C_1, Os, N_3, C_4 and C_{m1} (C_β) and C_{m3} (C_δ) of the porphodimethene core (Fig. 1). Thus, the macrocycle contains a pair of enantiotopic ethylidene groups (C_{m2} and C_5) and two methine carbons (C_{m1} and C_{m3}), each of which connects a set of two enantiotopic pyrrole rings. Only one atom of each set is labeled on the left hand side of Fig. 2. Although not required of the molecule in the crystal, the core of the molecule has approximate C_{2v} symmetry. Figure 3 displays average values of the bond lengths (C_{2v} symmetry) and radii of the core.

TABLE 1

ATOMIC COORDINATES IN THE UNIT CELL [a]

Atom type [b]	Coordinates		
	10^4x	10^4y	10^4z
Os [c]	639(0)	1/4	486(0)
O	—939(3)	1/4	—859(6)
N_1	383(2)	1903(1)	1902(3)
N_2	1087(2)	1902(1)	—771(3)
N_3	1842(2)	1/4	1415(4)
C_{a1}	289(2)	1993(2)	3308(3)
C_{a2}	338(2)	1369(2)	1694(4)
C_{a3}	998(2)	1366(1)	—641(3)
C_{a4}	1662(2)	1991(1)	—1766(3)
C_{b1}	168(2)	1482(2)	3959(4)
C_{b2}	192(2)	1094(2)	2959(4)
C_{b3}	1516(2)	1085(2)	—1541(4)
C_{b4}	1935(2)	1474(2)	—2246(4)
C_{m1}	261(3)	1/4	3898(5)
C_{m2}	409(2)	1111(2)	318(4)
C_{m3}	1913(3)	1/4	—2184(4)
C_1	—333(3)	1/4	—327(5)
C_2	2222(2)	2039(2)	1660(5)
C_3	2982(3)	2022(3)	2157(6)
C_4	3368(3)	1/4	2456(7)
C_5	—416(3)	1067(2)	—370(5)
C_{11}	—4(3)	1408(3)	5466(4)
C_{12}	—854(4)	1508(5)	5840(7)
C_{21}	106(4)	486(2)	3108(6)
C_{22}	858(5)	189(3)	3366(9)
C_{31}	1599(4)	481(2)	—1653(7)
C_{32}	2140(6)	253(3)	—570(12)
C_{41}	2544(2)	1393(2)	—3350(4)
C_{42}	2194(4)	1380(4)	—4764(6)

[a] The number in parentheses following each datum is the estimated deviation in the last significant figure. [b] Atoms are identified in agreement with Fig. 1. [c] For Os $10^5x = 6395(1)$, $10^5y = 25000(0)$, $10^5z = 4860(2)$.

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* These calculations followed ref. 13.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS [a]

Atom type	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os	2.33(0)	3.09(1)	2.18(0)	0.0(0)	0.21(1)	0.0(0)
O	3.6(2)	6.7(3)	6.4(2)	0.0(0)	−1.8(2)	0.0(0)
N_1	2.7(1)	4.0(1)	2.7(1)	−0.3(1)	0.1(1)	0.3(1)
N_2	2.9(1)	3.3(1)	2.8(1)	0.0(1)	0.3(1)	−0.2(1)
N_3	2.6(1)	5.0(2)	2.7(1)	0.0(0)	0.2(1)	0.0(0)
C_{a1}	2.8(1)	5.3(2)	2.8(1)	−0.1(1)	0.2(1)	0.8(1)
C_{a2}	3.1(1)	4.1(1)	3.7(1)	−0.8(1)	0.0(1)	0.7(1)
C_{a3}	3.3(1)	3.6(1)	3.3(1)	−0.2(1)	0.1(1)	−0.1(1)
C_{a4}	3.0(1)	3.6(1)	2.8(1)	0.2(1)	0.2(1)	−0.2(1)
C_{b1}	3.8(2)	6.0(2)	3.2(1)	−0.5(1)	0.1(1)	1.5(1)
C_{b2}	4.0(2)	5.0(2)	4.4(2)	−0.9(1)	−0.1(1)	1.8(1)
C_{b3}	4.0(2)	3.4(1)	4.8(2)	0.1(1)	0.2(1)	−1.0(1)
C_{b4}	3.4(1)	4.0(1)	3.7(1)	0.2(1)	0.2(1)	−0.9(1)
C_{m1}	3.3(2)	6.0(3)	2.3(2)	0.0(0)	−0.3(1)	0.0(0)
C_{m2}	3.9(1)	3.5(1)	4.0(2)	−0.6(1)	−0.1(1)	0.3(1)
C_{m3}	3.1(2)	3.6(2)	2.5(1)	0.0(0)	0.6(1)	0.0(0)
C_1	3.0(2)	4.2(2)	3.3(2)	0.0(0)	−0.1(2)	0.0(0)
C_2	3.6(2)	5.8(2)	5.0(2)	0.8(1)	−0.6(1)	0.6(2)
C_3	3.6(2)	9.3(4)	5.5(2)	2.0(2)	−0.2(2)	1.1(2)
C_4	2.2(2)	10.8(5)	4.7(3)	0.0(0)	−0.1(2)	0.0(0)
C_5	4.4(2)	6.2(2)	4.9(2)	−1.6(2)	−0.2(2)	0.1(2)
C_{11}	5.6(2)	8.1(3)	3.6(2)	−0.3(2)	0.4(2)	2.3(2)
C_{12}	6.6(3)	16.6(8)	5.4(3)	0.9(4)	2.5(2)	4.4(4)
C_{21}	7.5(3)	5.4(2)	5.8(2)	−2.4(2)	−0.5(2)	2.1(2)
C_{22}	11.3(5)	4.8(2)	9.5(4)	0.1(3)	−1.5(4)	2.0(3)
C_{31}	7.0(3)	3.7(2)	10.0(4)	−0.1(2)	2.3(3)	−1.7(2)
C_{32}	9.1(5)	5.3(3)	19.8(11)	2.5(3)	2.0(5)	3.6(4)
C_{41}	3.7(1)	5.2(2)	4.6(2)	0.5(1)	0.7(1)	−1.3(2)
C_{42}	6.3(3)	13.0(6)	4.5(2)	1.4(3)	1.1(2)	−2.2(3)

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. B_{ij} is related to the dimensionless β_{ij} employed during the refinement as $B_{ij} = 4\beta_{ij}/a_i^{*}a_j^{*}$.

TABLE 3

BOND LENGTHS IN THE COORDINATION GROUP, PORPHINATO SKELETON, CARBONYL LIGAND, AND PYRIDINE LIGAND [a]

Type	Length (Å)	Type	Length (Å)	Type	Length (Å)
$Os-N_1$	2.069(3)	$C_{m1}-C_{a1}$	1.379(5)	$C_{a4}-C_{b4}$	1.435(5)
$Os-N_2$	2.065(3)	$C_{m2}-C_{a2}$	1.493(6)	$C_{b1}-C_{b2}$	1.370(7)
$Os-N_3$	2.230(4)	$C_{m2}-C_{a3}$	1.507(5)	$C_{b3}-C_{b4}$	1.380(6)
$Os-C_1$	1.828(5)	$C_{m2}-C_5$	1.554(6)	C_1-O	1.151(7)
N_1-C_{a1}	1.401(4)	$C_{m3}-C_{a4}$	1.389(4)	N_3-C_2	1.329(5)
N_1-C_{a2}	1.337(5)	$C_{a1}-C_{b1}$	1.429(6)	C_2-C_3	1.377(6)
N_2-C_{a3}	1.337(5)	$C_{a2}-C_{b2}$	1.432(5)	C_3-C_4	1.381(8)
N_2-C_{a4}	1.395(4)	$C_{a3}-C_{b3}$	1.424(5)		

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure.

TABLE 4

BOND ANGLES IN THE COORDINATION GROUP, PORPHINATO SKELETON, CARBONYL LIGAND, AND PYRIDINE LIGAND[a]

Angle	Value (deg.)	Angle	Value (deg.)
N_1OsN_1'[b]	90.9(2)	$N_1C_{a2}C_{b2}$	110.2(3)
N_1OsN_2	88.0(1)	$C_{m2}C_{a2}C_{b2}$	126.2(4)
N_1OsN_2'	170.1(1)	$N_2C_{a3}C_{m2}$	123.2(3)
N_1OsN_3	85.4(1)	$N_2C_{a3}C_{b3}$	110.8(3)
N_1OsC_1	95.8(1)	$C_{m2}C_{a3}C_{b3}$	126.0(3)
N_2OsN_1'	170.1(1)	$N_2C_{a4}C_{m3}$	124.1(3)
N_2OsN_2'	91.3(2)	$N_2C_{a4}C_{b4}$	108.3(3)
N_2OsN_3	84.7(1)	$C_{m3}C_{a4}C_{b4}$	127.6(3)
N_2OsC_1	94.1(1)	$C_{a1}C_{m1}C_{a1}'$	130.3(5)
N_3OsC_1	178.3(5)	$C_{a2}C_{m2}C_{a3}$	115.8(3)
OsN_1C_{a1}	124.5(2)	$C_{a2}C_{m2}C_5$	110.4(4)
OsN_1C_{a2}	127.8(2)	$C_{a3}C_{m2}C_5$	110.8(3)
OsN_2C_{a3}	127.5(2)	$C_{a4}C_{m3}C_{a4}'$	129.8(4)
OsN_2C_{a4}	124.0(2)	$C_{a1}C_{b1}C_{b2}$	107.1(3)
OsN_3C_2	121.1(2)	$C_{a2}C_{b2}C_{b1}$	106.9(4)
OsC_1O	178.9(14)	$C_{a3}C_{b3}C_{b4}$	106.6(3)
$C_{a1}N_1C_{a2}$	107.5(3)	$C_{a4}C_{b4}C_{b3}$	106.9(3)
$C_{a3}N_2C_{a4}$	107.5(3)	$C_2N_3C_2'$	117.7(5)
$N_1C_{a1}C_{m1}$	124.0(3)	$N_3C_2C_3$	122.9(5)
$N_1C_{a1}C_{b1}$	108.2(3)	$C_2C_3C_4$	119.4(5)
$C_{m1}C_{a1}C_{b1}$	127.6(4)	$C_3C_4C_3'$	117.6(6)
$N_1C_{a2}C_{m2}$	123.6(3)		

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure. [b] C_i and C_i' represent atoms related by the mirror plane at $y = 1/4$.

The displacement of the skeletal carbon atoms from the mean plane of the four nitrogen atoms is given in Fig. 2. On the right hand side of the diagram, the symbol identifying each atom is replaced by the perpendicular displacement (in units of 0.01 Å) of this atom from the mean plane of the four nitrogen atoms The corresponding enantiotopic atoms on the left hand side of the diagram have displacements of the same magnitude and sign. As is usual, local flatness is preserved for each pyrrole ring with the maximum deviation from exact planarity being less than 0.008 Å. As expected, the core is folded along the line joining the two saturated *meso*-carbon atoms C_α and C_γ (C_{m2} and C_{m2}' of Fig. 1). The angle of 38.1° between the normals to the two pyrromethene halves (the mean plane of a pyrromethene half is defined by atom C_{m1}, the atoms of the adjoining pyrrole ring and the enantiotopic pyrrole ring or atom C_{m3}, the atoms of the adjoining pyrrole ring and the enantiotopic pyrrole ring) specifies the folding.

The value of the angle between the pyrromethene halves in the ruffled nickel complex, Ni(OEPMe$_2$) [14], is 52° and is 38.2° for the more comparable titanyl complex, TiO(OEPMe$_2$) [15]. The angle between the normals of the pyrrole rings defining a pyrromethene half are much smaller: 10.3° between pyrrole ring N_1 and the enantiotopic ring, and 1.1° between pyrrole ring N_2 and the enantiotopic ring.

The mean plane of the porphodimethene skeleton is approximately parallel to the mean plane of the four nitrogen atoms but is displaced by ~0.20 Å. Con-

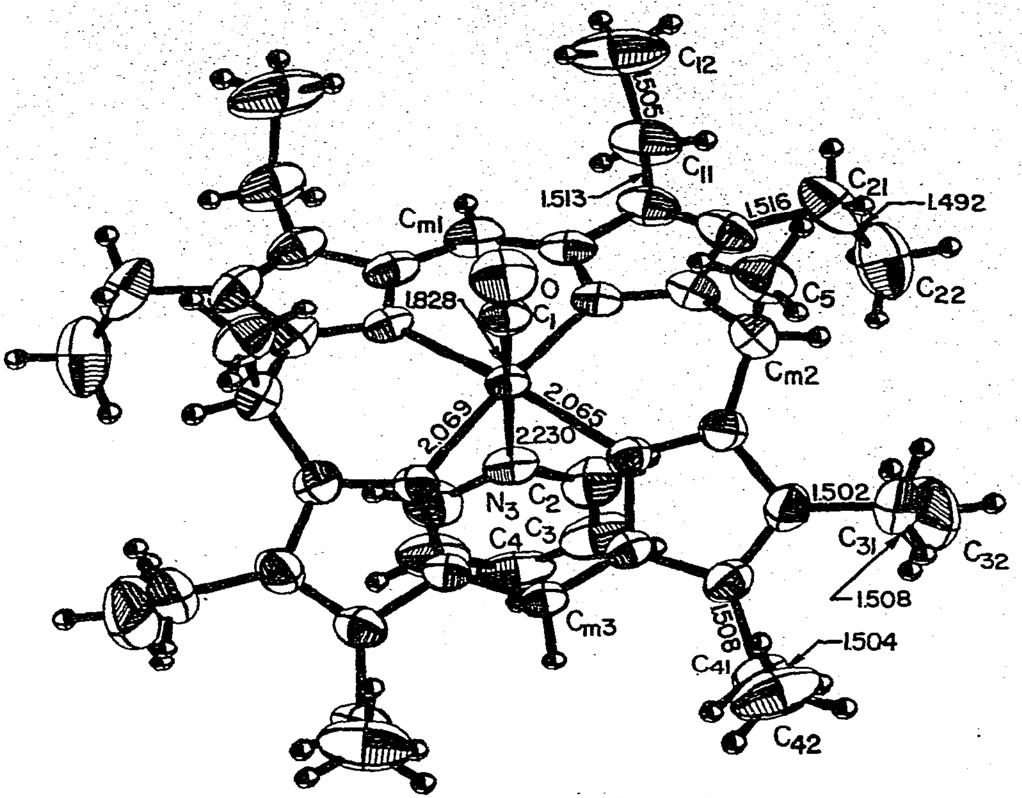

Fig. 1. Computer-drawn model in perspective of the Os(OEPMe$_2$)CO · Py molecule as it exists in the crystal. The crystallographically required mirror plane passes through atoms O, C$_1$, Os, C$_{m1}$, C$_{m3}$, N$_3$, and C$_4$. Observed bond distances for the coordination group and the peripheral ethyl groups are also displayed.

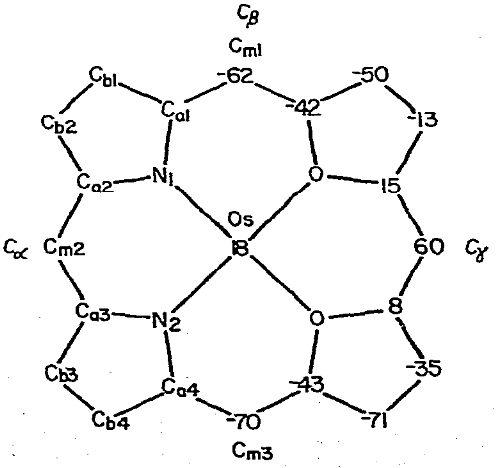

Fig. 2. A formal diagram of the porphodimethene core displaying, on the left hand side, the special symbols identifying each atom. On the right hand side of the diagram, the special symbol identifying each atom has been replaced by the perpendicular displacement of the atom, in units of 0.01 Å, from the mean plane of the four nitrogen atoms of the core. The displacement of the mirror-related atoms have the same magnitude and sign as those shown.

sequently, the displacement of individual atoms from the mean plane of the core can be obtained by adding 0.20 Å to the cited displacements given in Fig. 2. The osmium(II) ion is displaced 0.38 Å out of the mean plane of the porphodimethene core and 0.18 Å out of the plane of the four nitrogen atoms toward the carbonyl ligand, which is on the same side of the plane as the two methyl groups of the ethylidene groups (C_{m2} and C_5) which have the *syn*-axial configuration. The *syn*-axial configuration of the methyl groups appears to be the usual configuration, as it has been observed in all known structures of α,γ-dimethyl-α,γ-dihydrooctaethylporphin derivatives. In addition, the more firmly bound axial ligand, CO in this case, prefers the *syn*-position with respect to methyl groups and thus resides on the "ridge of the roof". Consequently, we expect the same configuration for Fe(OEPMe$_2$)CO · Py (IIa).

The Os—N bond distances of 2.065 (3) and 2.069 (3) Å are relatively long bond distances for a metal ion coordinated to porphyrin type ligands. These distances are nonetheless short relative to observed Os—NH$_3$ bond distances of 2.14 Å in [Os(NH$_3$)$_5$N$_2$]Cl$_2$ [16] and 2.136 (9) Å in [Os(NH$_3$)Cl$_3$(P(C$_6$H$_5$)$_3$)$_2$] [17]. With the above lengths as reference values, the Os—N$_{Py}$ bond length of 2.230 (4) Å appears long. Part of this lengthening may be ascribed to steric interaction between the α-hydrogen atoms of the pyridine ligand and atoms of the porphodimethene core: observed H···(porphodimethene core atom) contacts range from 2.69 Å upwards. The retention of the pyridine ligand throughout the course of the purification of Os(OEPMe$_2$)CO · Py is all the more remarkable considering the length of the Os—N$_{Py}$ bond.

The Os—C distance of 1.828 (5) Å is shorter than the average Os—C distances reported for Os$_3$(CO)$_{12}$ [18], bis-(μ-acetato)-hexacarbonyldiosmium [19] and [Os$_3$(CO)$_8$Ph$_4$C$_4$] [20] but within the range of values reported for these complexes.

Average bond distances and angles (C_{2v} symmetry) of the core are displayed in Fig. 3. The number in parentheses following each averaged value are, respectively, the mean deviation from the average and the estimated standard deviation

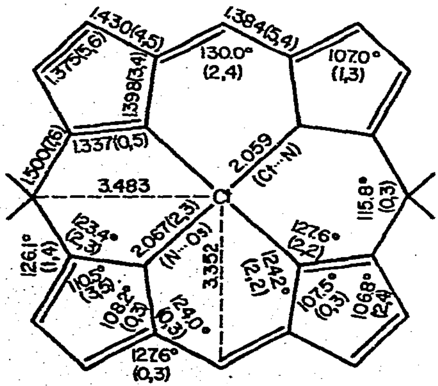

Fig. 3. A formal diagram of the porphodimethene core displaying averaged values of bond distances and angles (C_{2v} symmetry). The numbers in parentheses following each averaged value are, respectively, the mean deviation from the average and the estimated standard deviation of an individual value. Distances from the center of the four nitrogen atoms (Ct) to selected atoms are shown as are the two limiting Kekulé structures of each pyrromethene half (top and bottom).

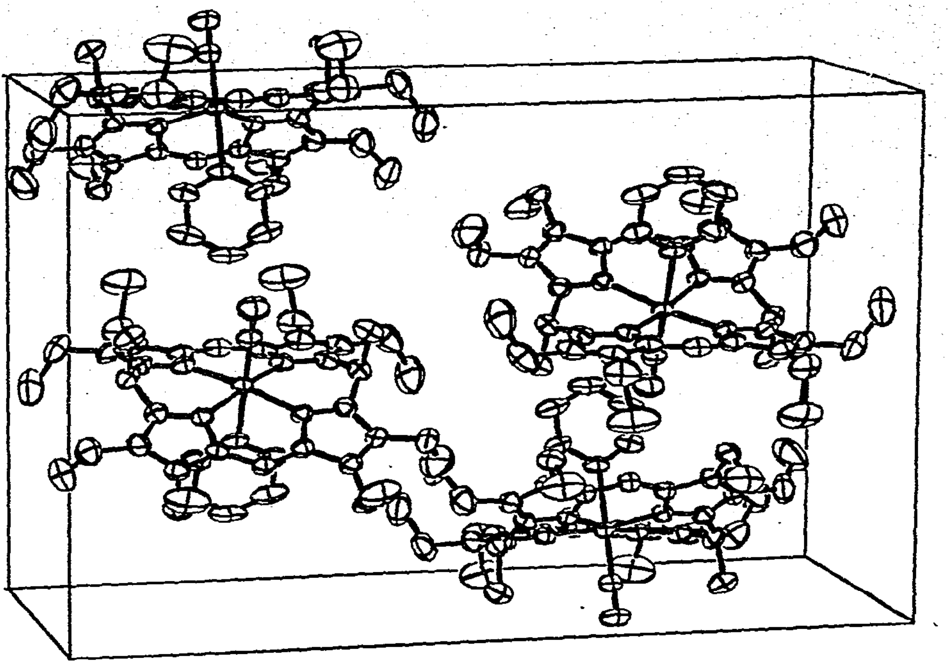

Fig. 4. A diagram illustrating the packing of the Os(OEPMe$_2$)CO · Py molecules in the unit cell.

of an individual bond length (or angle) in the last significant figure of the datum. Differences in the values for the two symmetry unique C—N bonds and deviations of the C—C bond lengths from values found for porphyrin derivatives have been previously discussed in terms of limiting Kekulé structures for π-electron delocalization in the porphodimethene core [14].

Fig. 4 displays the packing of the molecules in the unit cell. Intermolecular contacts range from 3.5 Å upwards; there are no unusually short intermolecular contacts.

Experimental section

Synthesis (J.W.B., K.L.L. and P.D.S.)

The starting material, Os(OEP)CO · Py (Ib), was prepared from octaethylporphyrin and OsO$_4$ as described previously [7]. The elemental analysis was performed by A. Bernhardt, D-5251 Elbach (West Germany).

Carbonyl(α,γ-dimethyl-α,γ-dihydrooctaethylporphinato)pyridineosmium(II); Os(OEPMe$_2$)CO · Py (IIb)

A suspension of 308 mg of Os(OEP)CO · Py (Ib) (0.37 mmole) in 100 ml of dry, oxygen-free THF was continuously stirred under a N$_2$ atmosphere in a 250-ml Schlenk tube. Five ml of 0.25 *M* sodium anthracenide in THF were injected dropwise with a syringe through a septum cap. After the colour had changed from red to green, 10 ml of dry, degassed methyl iodide were injected all at once. The solvent was removed from the resulting orange-brown solution under vacuum and the resulting residue was chromatographed three times on a silica gel plate (100 × 20 × 0.05 cm), developing with THF/cyclohexane (2 : 98). The product runs as an orange-brown band with R_F ~0.8, slightly behind the unreacted starting material, Os(OEP)CO · Py. The product was removed from the adsorbent with CH_2Cl_2 and crystallized from 20 ml of CH_2Cl_2/MeOH (3 : 1) as dark brown, crystalline plates. Suction filtration, thorough washing with methanol and drying at 70°C/10^{-2} mm Hg for 12 h yielded 60 mg (19%) Os($OEPMe_2$)CO · Py (IIb).

Elemental analysis: Found: C, 60.62; H, 6.60; N, 8.49; O, 1.97. $C_{44}H_{55}N_5OOs$ (859.2) calcd.: C, 61.44; H, 6.44; N, 8.14; O, 1.86%.

Spectral characterization

Electronic absorption spectrum (Unicam SP 800 B, benzene): λ_{max} (log ϵ) = 439 (4.79). *Infrared spectrum* (Perkin—Elmer 621, KBr): $\tilde{\nu}$(CO) = 1863 cm^{-1}, characteristic absorption bands for the $(OEPMe_2)^{2-}$ ligand are found at 1592, 1224, 998 and 864 cm^{-1}.

^1H NMR spectrum (Jeol JNM-C-60 HL, $CDCl_3$): δ = 1.13 (t, C_2H_5); 1.30 (t, C_2H_5); 1.62 (m, Py); 1.85 (d, CH_3); 2.60 (q, C_2H_5); 2.64 (q, C_2H_5); 4.59 (q, CH-α,γ); 6.66 (s, CH-β,δ); 6.90 (m, Py).

Mass spectrum (Varian CH5): A = 782 [45%, ^{192}Os($OEPMe_2$)CO^+], 767 [64%, Os(OEPMe)CO^+], 752 [100%, Os(OEP)CO^+], 738 [19%, Os(OEPMe − C_2H_5)CO^+], 724 [91%, $Os(OEP)^+$], 391 [20%, Os($OEPMe_2$)CO^{2+}], 383.5 [4%, $Os(OEPMe)^{2+}$], 376 [8%, Os(OEP)CO^{2+}], 369 [14%, Os(OEPMe − C_2H_5)CO^{2+}], 362 [34%, $Os(OEP)^{2+}$], 79 [Py^+].

Determination of the crystal and molecular structure (W.R.S., G.A.R. and J.E.K.)

Preliminary X-ray examination established an orthorhombic four-molecule unit cell with $Pn2_1a$ or $Pnma$ as the possible space groups. Lattice constants a 16.937 (1) Å, b 24.694 (2) Å, and c 9.778 (1) Å (0.71069), came from a least-squares refinement that utilized the setting angles of 26 reflections, each collected at $\pm 2\theta$. These constants led to a calculated density at 20 ± 1° of 1.397 g/cm^3 for a cell content of $4OsON_5C_{44}H_{55}$; the observed density is 1.39 g/cm^3.

Intensity data were measured on a Syntex $P\bar{1}$ diffractometer using the θ—2θ scanning technique with graphite-monochromated Mo-K_α radiation. Data collection techniques were essentially those described previously [21]. Four standard reflections were monitored periodically and no crystal decomposition was noted. All independent data having ($\sin\theta/\lambda$) $\leqslant 0.708$ Å^{-1} were measured. The dimensions of the crystal used in data collection was 0.250 × 0.417 × 0.602 mm in the three largest dimensions and was bounded by $\{1,0,0\}$, $\{0,1,0\}$, $\{0,1,1\}$ and $\{0,\bar{1},1\}$. With a linear absorption coefficient of 3.099 mm^{-1}, an absorption correction was deemed necessary. The minimum and maximum transmission coefficients were 0.460 and 0.652, respectively.

The net intensities were reduced to a set of relative squared amplitudes as described previously [21]; all data having $F_0 < 3\sigma(F_0)$ were taken to be unobserved; 4644 independent data were considered observed (76% of the theoretical number possible). Only the observed data were used for the determination and refinement of structure.

With four molecules per unit cell, the choice of *Pnma* requires that the molecule has C_s symmetry; the choice of the space group $Pn2_1a$ leads to no required symmetry for the molecule. The initial choice of *Pnma* as the space group was fully confirmed by all subsequent developments during the determination and refinement of structure. The structure was solved by the standard heavy-atom method. Block-diagonal least-squares refinement * was followed by a difference Fourier synthesis which revealed electron density concentrations appropriately located for all hydrogen atoms. The positions of the hydrogen atoms were idealized (C—H = 0.95 Å) and included in the subsequent refinement cycles as fixed contributors. The refinement was then carried to convergence using anisotropic thermal parameters for all heavy atoms. The final value of $R_1 = \Sigma|F_0| - |F_e|/\Sigma|F_0|$ was 0.031, that of $R_2 = [\Sigma w(|F_0| - |F_e|)^2/\Sigma w(F_0)^2]^{1/2}$ was 0.038. The estimated standard deviation of an observation of unit weight was 1.158. The final parameter shifts were less than 20% of the estimated standard deviation during the last cycle. A final difference Fourier synthesis had some features close to the Os atom but was otherwise featureless.

Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables 1 and 2, respectively. Primed and unprimed symbols, e.g., C_i and C_i', denote a pair of atoms related by the mirror plane of symmetry (see Fig. 3).

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* The program, REFINE, written by J.J. Park at Cornell University. The function minimized was $\Sigma w(|F_0| - s|F_e|)^2$ wherein w is the weight and s is the scaling factor. Atomic form factors were from ref. 22, with corrections, real and imaginary, for the anomalous scattering of the osmium atom from ref. 23.

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