

The Crystal Structure of Octaethylporphinato(methyl)rhodium(III). An Unusually Short Rh–CH₃ Distance

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Triclinic, $P\bar{1}$, $a=15.891(10)$, $b=10.890(4)$, $c=10.753(1)$ Å, $\alpha=100.96(2)$, $\beta=95.44(3)$, $\gamma=59.53(3)^\circ$, $C_{37}H_{47}N_4Rh$, $Z=2$, $D_m=1.37$, $D_x=1.37$ g cm⁻³, $\mu(\text{Cu } K\alpha)=49.0$ cm⁻¹. The Rh atom in the metalloporphyrin is coordinated in a square-pyramidal way by porphyrinato nitrogen atoms and a methyl group, and lies on the basal plane of the four nitrogen atoms.

The title compound, obtained from a reaction of *N*-methyloctaethylporphine and [Rh(CO)₂Cl]₂ (Ogoshi, Omura & Yoshida, 1973), was recrystallized from CH₂Cl₂–C₆H₆ at about 35°C (triclinic crystals with density of 1.33 g cm⁻³ were obtained at room temperature). The unit-cell parameters were determined by least-squares calculations from Weissenberg photographs about the three axes, calibrations being made with superposed Si lines. Three-dimensional intensities were recorded on integrated Weissenberg photographs with Cu *K*α radiation and measured by a TV densitometer (Izumi, 1971). Two crystals of dimensions 0.08 × 0.12 × 0.17 mm and 0.11 × 0.15 × 0.45 mm were used for *b*- and *c*-axis rotations respectively. Corrections were made for Lorentz and polarization effects and for spot size (Takenaka & Sasada, 1973), but not for absorption. Two series of relative intensities were then cross-correlated. The number of independent reflexions was 5307, of which 4186 were non-zero reflexions.

The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculations (first isotropic and then anisotropic), using the non-zero reflexions. The function minimized was $\sum w\Delta^2$ ($\Delta=|F_o|-|F_c|$). All the hydrogen atoms were found on

a difference map and included in further refinements. The weighting scheme applied was $w=\exp(as^2+bt^2+cs+ds+et+f)$, where $s=|F_o|\times 10^{-2}$ and $t=\sin\theta/\lambda$. For each cycle of the refinement, the coefficients, a , b , c , d , e , and f , were evaluated by a least-squares fit so that $\langle w\Delta^2 \rangle = 1$; their values at the final cycle were -1.141 , -16.07 , -6.972 , -2.047 , 13.57 , and -2.156 , respectively. The final R was 0.052.

Atomic scattering factors used were those of the neutral atoms given in *International Tables for X-ray Crystallography* (1962). The final atomic parameters are given in Table 1. Bond distances and angles are given in Table 2.* A stereoscopic view of the molecule is shown in Fig. 1 together with the atomic numbering.

Discussion

As shown in Fig. 1, the methyl group is at the apex of a square pyramid and the four nitrogen atoms form a basal plane. The Rh–N distance, 2.031 Å on average,

* Tables of observed and calculated structure factors and of bond distances and angles involving the hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31129 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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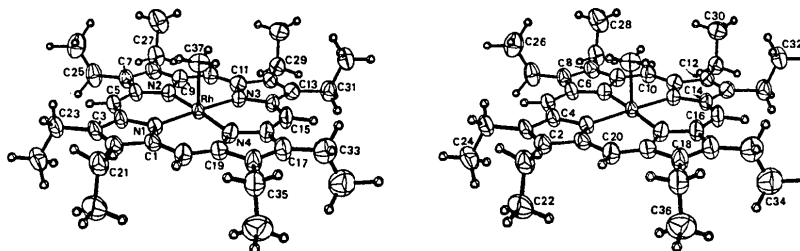


Fig. 1. Stereoscopic drawing of the molecule of octaethylporphinato(methyl)rhodium(III). The non-hydrogen atoms are represented by their thermal ellipsoids scaled to include 50% probability, while the hydrogen atoms are represented by an arbitrary size.

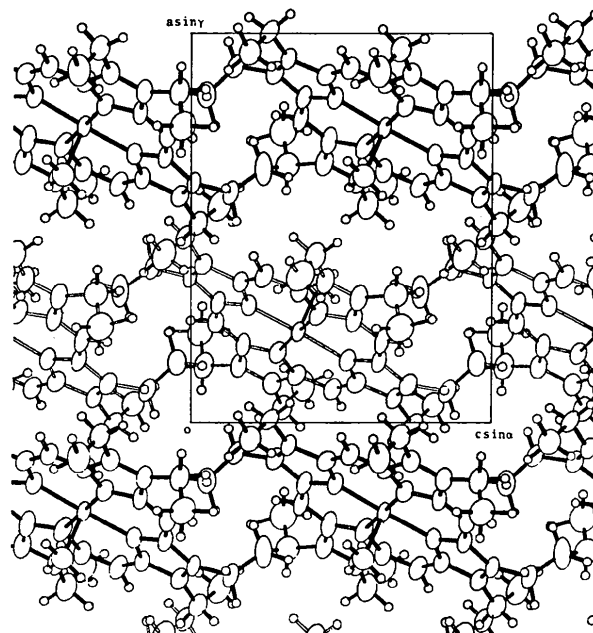
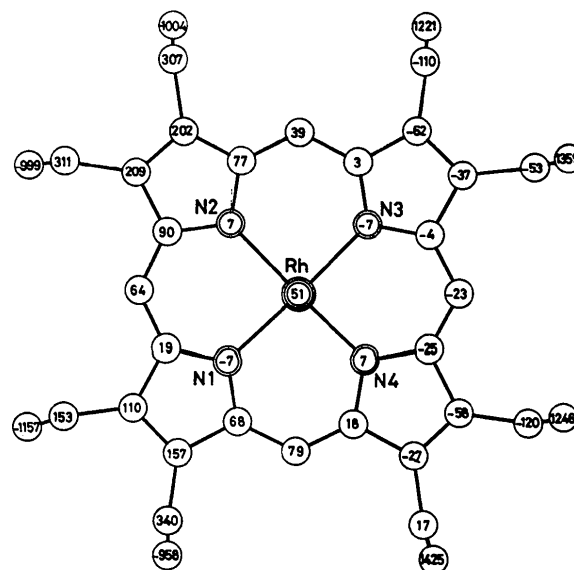
Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Rh—C(37)	2.031 (6)	C(11)—C(12)	1.455 (8)
Rh—N(1)	2.022 (5)	C(13)—C(14)	1.456 (10)
Rh—N(2)	2.041 (6)	C(16)—C(17)	1.466 (13)
Rh—N(3)	2.025 (5)	C(18)—C(19)	1.470 (10)
Rh—N(4)	2.036 (6)	C(2)—C(3)	1.361 (10)
N(1)—C(1)	1.379 (9)	C(7)—C(8)	1.352 (9)
N(1)—C(4)	1.391 (7)	C(12)—C(13)	1.352 (10)
N(2)—C(6)	1.358 (7)	C(17)—C(18)	1.354 (10)
N(2)—C(9)	1.375 (10)	C(2)—C(21)	1.492 (12)
N(3)—C(11)	1.380 (10)	C(3)—C(23)	1.497 (8)
N(3)—C(14)	1.375 (7)	C(7)—C(25)	1.492 (10)
N(4)—C(16)	1.363 (7)	C(8)—C(27)	1.514 (13)
N(4)—C(19)	1.380 (10)	C(12)—C(29)	1.511 (11)
C(4)—C(5)	1.365 (11)	C(13)—C(31)	1.509 (8)
C(5)—C(6)	1.387 (10)	C(17)—C(33)	1.522 (10)
C(9)—C(10)	1.365 (8)	C(18)—C(35)	1.512 (14)
C(10)—C(11)	1.392 (9)	C(21)—C(22)	1.522* (11)
C(14)—C(15)	1.390 (12)	C(23)—C(24)	1.526* (10)
C(15)—C(16)	1.385 (11)	C(25)—C(26)	1.521* (9)
C(19)—C(20)	1.361 (8)	C(27)—C(28)	1.554* (12)
C(20)—C(1)	1.392 (9)	C(29)—C(30)	1.538* (10)
C(1)—C(2)	1.459 (8)	C(31)—C(32)	1.532* (9)
C(3)—C(4)	1.450 (9)	C(33)—C(34)	1.491* (10)
C(6)—C(7)	1.455 (11)	C(35)—C(36)	1.501* (12)
C(8)—C(9)	1.453 (10)		

C(37)—Rh—N(1)	90.4 (3)	C(10)—C(9)—C(8)	125.5 (7)
C(37)—Rh—N(2)	93.1 (3)	C(10)—C(11)—C(12)	125.2 (7)
C(37)—Rh—N(3)	92.1 (3)	C(15)—C(14)—C(13)	125.7 (5)
C(37)—Rh—N(4)	90.2 (3)	C(15)—C(16)—C(17)	125.1 (6)
N(1)—Rh—N(2)	89.9 (2)	C(20)—C(19)—C(18)	125.3 (7)
N(2)—Rh—N(3)	89.8 (2)	C(4)—C(5)—C(6)	128.4 (5)
N(3)—Rh—N(4)	89.8 (2)	C(9)—C(10)—C(11)	126.7 (7)
N(4)—Rh—N(1)	90.3 (2)	C(14)—C(15)—C(16)	126.9 (6)
N(1)—Rh—N(3)	177.5 (2)	C(19)—C(20)—C(1)	126.6 (8)
N(2)—Rh—N(4)	176.7 (2)	C(1)—C(2)—C(3)	106.8 (6)
Rh—N(1)—C(1)	126.4 (4)	C(4)—C(3)—C(2)	107.1 (5)
Rh—N(1)—C(4)	127.2 (4)	C(6)—C(7)—C(8)	106.9 (6)
Rh—N(2)—C(6)	126.2 (4)	C(9)—C(8)—C(7)	107.2 (7)
Rh—N(2)—C(9)	126.2 (4)	C(11)—C(12)—C(13)	106.6 (6)
Rh—N(3)—C(11)	127.0 (4)	C(14)—C(13)—C(12)	107.2 (5)
Rh—N(3)—C(14)	127.2 (4)	C(16)—C(17)—C(18)	106.2 (6)
Rh—N(4)—C(16)	126.7 (4)	C(19)—C(18)—C(17)	107.8 (8)
Rh—N(4)—C(19)	125.5 (4)	C(1)—C(2)—C(21)	125.2 (6)
C(1)—N(1)—C(4)	105.8 (5)	C(4)—C(3)—C(23)	125.2 (7)
C(6)—N(2)—C(9)	107.6 (6)	C(6)—C(7)—C(25)	125.3 (7)
C(11)—N(3)—C(14)	105.8 (5)	C(9)—C(8)—C(27)	124.7 (6)
C(16)—N(4)—C(19)	107.5 (6)	C(11)—C(12)—C(29)	125.0 (6)
N(1)—C(1)—C(2)	110.2 (5)	C(14)—C(13)—C(31)	124.9 (7)
N(1)—C(4)—C(3)	110.1 (6)	C(16)—C(17)—C(33)	125.4 (7)
N(2)—C(6)—C(7)	109.4 (6)	C(19)—C(18)—C(35)	125.3 (6)
N(2)—C(9)—C(8)	108.8 (5)	C(3)—C(2)—C(21)	128.0 (5)
N(3)—C(11)—C(12)	110.3 (6)	C(2)—C(3)—C(23)	127.7 (7)
N(3)—C(14)—C(13)	110.1 (6)	C(8)—C(7)—C(25)	127.8 (8)
N(4)—C(16)—C(17)	110.1 (6)	C(7)—C(8)—C(27)	128.0 (6)
N(4)—C(19)—C(20)	108.4 (5)	C(13)—C(12)—C(29)	128.4 (5)
N(1)—C(1)—C(20)	124.7 (5)	C(12)—C(13)—C(31)	127.9 (7)
N(1)—C(4)—C(5)	123.1 (6)	C(18)—C(17)—C(33)	128.3 (9)
N(2)—C(6)—C(5)	124.9 (7)	C(17)—C(18)—C(35)	126.9 (7)
N(2)—C(9)—C(10)	125.7 (6)	C(2)—C(21)—C(22)	115.0 (6)
N(3)—C(11)—C(10)	124.5 (6)	C(3)—C(23)—C(24)	114.2 (5)
N(3)—C(14)—C(15)	124.2 (6)	C(7)—C(25)—C(26)	114.7 (6)
N(4)—C(16)—C(15)	124.9 (8)	C(8)—C(27)—C(28)	112.4 (7)
N(4)—C(19)—C(20)	126.1 (7)	C(12)—C(29)—C(30)	113.4 (5)
C(20)—C(1)—C(2)	125.1 (7)	C(13)—C(31)—C(32)	113.4 (5)
C(5)—C(4)—C(3)	126.9 (5)	C(17)—C(33)—C(34)	110.4 (7)
C(5)—C(6)—C(7)	125.7 (5)	C(18)—C(35)—C(36)	114.7 (7)

* Corrected for riding motion.

is in good agreement with that (2.038 Å) in the octahedral Rh(III)-porphyrin (Hanson, Gouterman & Hanson, 1973). Closer examination shows that the two adjacent Rh—N distances differ slightly from each other. A similar difference has also been observed in the octahedral Rh(III)-porphyrin mentioned above. The bond distances and angles in the porphyrin moiety are close to those found in the other metallo-

Fig. 2. The crystal structure of octaethylporphinato(methyl)rhodium(III), viewed down the *b* axis.Fig. 3. Deviations ($\times 10^3$ Å) of the non-hydrogen atoms from the mean plane which is expressed by $-0.4599X + 0.8096Y - 0.3649Z = 1.875$ through the four nitrogen atoms (*X*, *Y*, and *Z* are in Å along the directions, *a*, *c** \times *a*, and *c**, respectively). The methyl carbon atom is 2.082 Å from the plane.

porphyrins (see *e.g.* Collins, Scheidt & Hoard, 1972; Little & Ibers, 1974a). The conformations of the peripheral ethyl groups are also similar to those of other complexes with octaethylporphine (see *e.g.* Cullen & Meyer, 1974; Takenaka, Sasada, Ogoshi, Omura & Yoshida, 1975). The molecules are packed in the crystal through van der Waals contacts between the aromatic planar parts and between the aliphatic groups (see Fig. 2). The two methylenic hydrogen atoms of the neighbouring molecule approach the rhodium atom on the opposite side of the methyl group, the Rh...H distances being 2.89 and 3.24 Å. There are no abnormally short intermolecular contacts.

Fig. 3 shows the deviations of atoms from the mean plane through the four nitrogen atoms. It should be noted that the deviation of Rh is only 0.051 Å from the mean plane toward the apex. In the usual square pyramid of Co-, Zn-, and Fe-porphyrins (Scheidt, 1974; Little & Ibers, 1974b; Dwyer, Madura & Scheidt, 1974; Collins & Hoard, 1970; Spaulding, Eller, Bertrand & Felton, 1974; Koenig, 1965; Hoard, Hamor, Hamor & Caughey, 1965; Hoffman, Collins, Day, Fleischer, Srivastava & Hoard, 1972; Hoard & Scheidt, 1973), the metal deviation increases with the bond radius of the metal. If this relation were applicable to the present complex, the Rh atom would have a deviation of 0.23–0.37 Å. This is not the case and the small deviation observed suggests that the metal is substantially on the basal plane; the eight bond angles of Rh are all very close to 90° and the diagonal N–Rh–N angles are near 180°. The present complex has, therefore, a square pyramid different from those so far found.

In the usual square pyramid of d^6 -metal complexes, the bond orbitals of metal have been considered to be d^2sp^2 hybrids. In the present configuration, however, it seems that the apical bond of Rh consists of the essentially pure $4d_{z^2}$ orbital and the other four bonds are due to the square planar $4d5s5p^2$.^{*} This is consistent with the fact that the Rh–C(methyl) distance (2.031 Å) is considerably shorter than that (2.081 Å) found in the usual square-pyramidal Rh(III) complex (Troughton & Skapski, 1968).

In the process of forming an octahedron by adding

* A similar argument has been put forward for the highly constrained molecule, in which the almost pure p_z orbital on an sp^2 hybridized carbon atom is forced to form a C–C bond (Wiberg, Burgmaier, Shen, La Placa, Hamilton & Newton, 1972).

a sixth ligand to the usual penta-coordinated complexes, it has been assumed that a square pyramid, in which the metal lies on the basal plane, is produced as an intermediate (Hoffmann, Chen, Elian, Rossi & Mingos, 1974). The present structure may be a model of such an intermediate.

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