Crystal Structure of μ-Octaethylporphinato-bis[dicarbonylrhodium(I)]

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Summary It is shown by *X*-ray analysis that the two Rh^I atoms in the title metalloporphyrin are located above and below the macrocyclic plane, the co-ordination of each metal being square planar.

Several kinetic studies on the formation of metalloporphyrins have suggested that the 'sitting-atop' metal ion deforms the porphyrin so as to facilitate the incorporation of the other ion.[1] The Re^I complex in which two metal atoms are co-ordinated to the porphyrin[2] might be used as a structural model for such an intermediate when the metal ion assumes octahedral co-ordination. A crystallographic study of analogues containing metals with different co-ordination has been performed to examine whether or not there are different modes of deformation of the porphyrin, and it has provided a further stereochemical basis for the mechanism of metal insertion.

μ-Octaethylporphinato-bis[dicarbonylrhodium(I)]† was recrystallized from $CHCl_3$–C_6H_6. *Crystal data:* $C_{40}H_{44}N_4O_4Rh_2$, space group $P2_1/c$, $a = 8{\cdot}778(2)$, $b = 12{\cdot}145(2)$, $c = 19{\cdot}134(3)$ Å, $\beta = 108{\cdot}94(2)°$, $D_m = 1{\cdot}46$, $D_c = 1{\cdot}464$ g cm^{-3}, $Z = 2$.

Three dimensional intensity data were collected on Weissenberg photographs and measured by a TV densitometer.[3] Of 3980 possible reflections (Cu-K_α radiation), 1135 were too weak to be observed. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares. The final R factor was 0·062.

As shown in the Figure, the two Rh^I atoms are co-ordinated to the porphyrin above and below the macrocyclic plane, similar to the Re^I complex.[2] Each Rh atom, however, has square-planar co-ordination; two nitrogen atoms of the four pyrrole rings and two carbonyl carbon atoms are co-ordinated to one Rh atom [Rh–N(1) 2·078(8), Rh–N(2) 2·087(7), Rh–C(19) 1·837(10) and Rh–C(20) 1·856(11) Å] and they are coplanar to within ±0·005 Å. This is the first example of metalloporphyrin systems in which two monovalent metal atoms form square-planar co-ordination with the porphyrin.

The Rh atom deviates, by 0·105 Å, from the basal plane toward the mid-point of the two nitrogen atoms co-ordinated to another Rh; Rh · · · N(1′) 3·058(8) Å and Rh · · · N(2′) 3·080(7) Å. There might be some interaction between these nitrogen and the monovalent rhodium atoms.

The average length of the chemically and structurally equivalent bonds is 1·36 for C_α–N, 1·44 for C_α–C_β, 1·36 for C_β–C_β, and 1·40 Å for C_α–C_m. The porphyrin ring is considerably deformed, so that the adjacent pyrrole rings, each of which is almost planar, form an angle of 19·1°. The distortion of the porphyrin ring causes asymmetry in the bond angles, *e.g.* 123·0 and 130·5° for C(4)–C(5)–C(6) and C(9)–C(10)–C(1′), respectively.

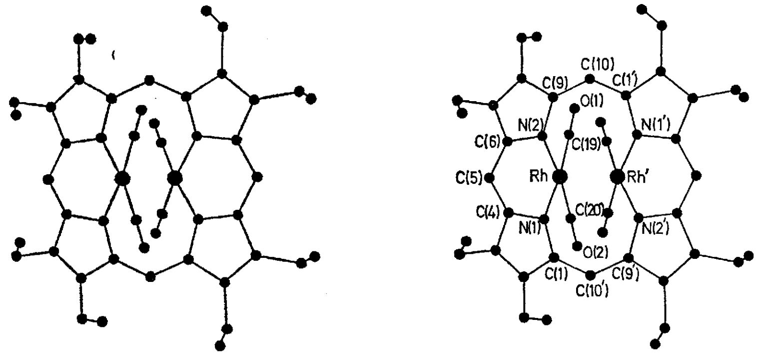

Figure. Stereoscopic view of the molecule of μ-octaethylporphinato-bis[dicarbonylrhodium(I)].

It has been proposed that the 'sitting-atop' metal ion binds to two nitrogen atoms in the aza-type pyrrole rings which are centrosymmetrically situated around the centre of the porphyrin. When the metal atom assumes square-planar co-ordination, however, the distance between the opposite nitrogen atoms seems to be too long. The present result shows that the nitrogen atoms in adjacent pyrrole rings are co-ordinated to one metal atom. In free-base porphyrins,[5] the inner hydrogen atoms are found to bond to the opposite two nitrogen atoms. Therefore, it may be supposed that formation of an intermediate with square-planar co-ordination causes release of one of the two

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† Prepared by the method used previously for (oep)[$Rh_2(CO)_4Cl$]H.[4] In the present study, the latter showed a strong tendency to liberate HCl in organic solvents.

hydrogen atoms. Such a proton release has been postulated as a stage in the reaction in kinetic studies on the formation of metalloporphyrins.[1]

Although the present Rh^{I} complex is stable to air in the crystalline state, it is oxidized in refluxing chloroform to the trivalent rhodium complex in which one metal ion is bonded to the porphyrin molecule.[4,6] In this process, one of the two metal atoms might migrate to the centre of the porphyrin. The present structure may thus be the 'sitting-atop' intermediate.

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