# Unusual Metalloporphyrins. Structure of the Product from the reaction of Dodecacarbonylruthenium with *meso*-Tetraphenylporphine: 'Dicarbonyltetraphenylporphinatoruthenium(II)'

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*Summary* The product of a reaction of $Ru_3(CO)_{12}$ and *meso*-tetraphenylporphine, previously believed to be an ethanol adduct of a monocarbonyl derivative of ruthenium(II) tetraphenylporphine, has been found by a single crystal *X*-ray analysis to be a centrosymmetrical octahedral complex of dicarbonyltetraphenylporphinatoruthenium (II).

THE monocarbonyl derivative of ruthenium(II) *meso*-tetraphenylporphine (I) has drawn the attention of several bioinorganic chemists[1-6] because a sixth ligand can add and form a weak adduct. Addition of a further ligand to (I) has obvious relevance to the understanding of the hemoproteins.[7] Two syntheses of (I) have been reported independently.[1-3] The initial product, from the reaction of $Ru_3(CO)_{12}$ and $H_2$ tpp (tpp = *meso*-tetraphenylporphine dianion) in benzene or toluene was believed to be (I) which later picks up a solvent molecule (ethanol, *etc.*) as a sixth ligand. In the case of a monocarbonyl derivative of ruthenium(II) mesoporphyrin IX dimethyl ester (II) the sixth ligand can be occupied by the ester carbonyl oxygen, a conclusion supported by i.r. spectroscopy in the solid state.[1,2] A single crystal *X*-ray diffraction analysis on a compound originally believed to be (I), with EtOH as sixth ligand, has now revealed that it is, in fact, dicarbonyl *meso*-tetraphenylporphinatoruthenium(II) (III). One of the carbonyl groups of (III) can be easily substituted in benzene solution with an imidazole giving an imidazole complex[1,2] of monocarbonyltetraphenylporphinatoruthenium(II) (IV).

Compound (III) was prepared by a procedure similar to that used previously,[1,2] with toluene instead of benzene as solvent and 12 h refluxing of the reaction mixture. The product was chromatographed with benzene–chloroform on neutral alumina and recrystallized from chloroform–ethanol: $\lambda_{max}$ ($CHCl_3$), two main peaks at 412 (Soret) and 529 nm, and a weak peak at 561 nm; $\nu_{max}$ ($CHCl_3$) 1941s $cm^{-1}$. A carbonyl i.r. stretch in this compound could be due to the presence of either one carbonyl group as previously reported,[1-3] or due to a symmetric arrangement of two carbonyl groups. The mass spectrum of (III) [*m/e* 770 ($M^+$) 742 ($M^+$ – CO) and 714 ($M^+$ – 2CO)] supports the presence of two carbonyl groups. The mass spectrum of (IV) shows the highest mass peak at *m/e* 742 ($M^+$) and another peak at *m/e* 714 ($M^+$ – CO) supporting the presence of only one carbonyl group in (IV).

An *X*-ray crystallographic analysis of a small single crystal (*ca.* 0·2 mm cross section) (III) (from $CHCl_3$–EtOH) was carried out. *Crystal data:* $C_{46}H_{28}N_4O_2Ru$; $M = 769·8$; space group $P1$ or $P\bar{1}$; $a = 10·097(3)$, $b = 11·849(3)$, $c = 8·865(4)$ Å, $\alpha = 101·30(3)$, $\beta = 105·89(4)$, $\gamma = 65·82(4)°$; $U = 926·3$ Å$^3$; $Z = 1$; $D_c = 1·380$; $D_m = 1·38$ g cm$^{-3}$; $\mu$ for (Mo-$K_\alpha$) 4·64 cm$^{-1}$.

Three-dimensional intensity data were collected on a Datex–Syntex automated diffractometer using pyrolitic-graphite-monochromatized Mo-$K_\alpha$ radiation ($\lambda = 0·71069$ Å). Data were collected to $2\theta = ca.$ 45°. Because of the small size of the crystal very few reflections could be observed beyond this point. A total of 2342 independent reflections were measured, of which 1526 were considered observed.

The structure was solved by Fourier techniques, principally using $\Delta F$ Fourier syntheses. All 27 non-hydrogen atoms and 13 of the 14 hydrogen atoms were located in this manner. The position of the fourteenth hydrogen atom, H(8), was calculated.

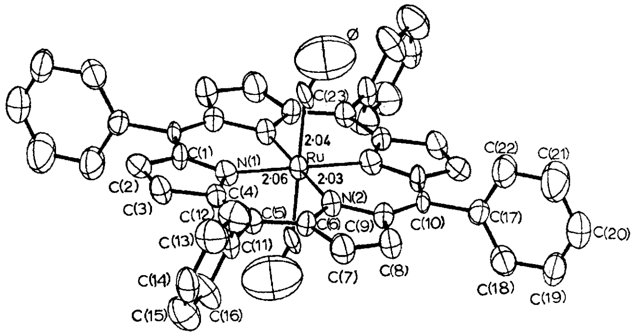

FIGURE. *ØRTEP*[9] *drawing of structure of dicarbonyl-*meso-*tetraphenylporphinatoruthenium*(II). *Thermal ellipsoids are drawn for* 50% *probability. Numbering scheme for half of the centrosymmetric molecule is shown.*

Attempts were made to distinguish between the carbon and oxygen atoms of the carbonyl ligand by integration of the peaks in the difference Fourier maps, but this test was inconclusive, largely because of the diffuse nature of the peak furthest from the ruthenium ion. However, the i.r. spectrum of (III) has already strongly suggested that the bonding is through the carbon atom.

The structure was refined by block-diagonal least-squares, followed by a final cycle of full-matrix least-squares refinement, to the present discrepancy indices of $R = 0·123$ and weighted $R = 0·090$, based on $F^2$. The conventional $R$ value based on $F$ is 0·086. Anisotropic thermal motion was assumed for all atoms except hydrogen for which isotropic thermal motion was used.

The metalloporphyrin is a centrosymmetric, slightly distorted octahedral complex. The structure is shown in the Figure. The two independent Ru–N distances are 2·06(1) and 2·03(1) Å, while the Ru–C(23) bonding distance is 2·04(1) Å. The average bond distances and their r.m.s. deviations are: C (methine) – $C_\alpha$ = 1·42(2), $C_\alpha$ – $C_\beta$ = 1·43(1), $C_\beta$ – $C_\beta$ = 1·36(1), and $C_\alpha$ – N = 1·38(1).

The bond angle N(1)–Ru–N(2) is 89·1°. The two N–Ru–C(23) bond angles are 91·6(4)° and 87·7(4)°, differing significantly from the ideal octahedral angle of 90°. The other bond angle of special note is Ru–C(23)–O [153·3(9)°] showing that the carbonyl molecule is not bonded linearly to the metal ion.

The porphyrin macrocycle is only very slightly ruffled, with an angle of 4·9° between adjacent pyrrole rings. As is found in all tetraphenylporphine complexes thus far studied, the phenyl rings are tilted from the plane of the porphyrin.[8] In this case phenyl ring 1 [C(11)–C(16)] is tilted 77·2° from the plane of the four pyrrole nitrogen atoms, while phenyl ring 2 [C(17)–C(22)] is tilted by 88·9°.

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