The First X-Ray Crystal and Molecular Structure of a Six-Coordinate Ruthenium(II) Octaethylporphyrin Carbonyl Complex, (OEP)Ru(CO)(H_2O)

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(OEP)Ru(CO)(H_2O) was characterized by X-ray crystallography and provides the first structure of a six-coordinate ruthenium(II) octaethylporphyrin carbonyl complex. Single-crystal X-ray analysis shows the complex to crystallize in the triclinic space group $P\bar{1}$ with cell constants a = 10.212 (2) Å, b = 13.717 (4) Å, c = 13.984 (3) Å, α = 114.72 (2)°, β = 104.58 (2)°, γ = 90.15 (2)° and Z = 2. The central ruthenium ion has an axially distorted octahedral geometry and the distances between the central metal and axial ligands are 1.785 (4) Å for Ru-C and 2.253 (2) Å for Ru-O. The ruthenium atom is displaced out of the porphyrin plane by 0.14 Å towards CO, with an average Ru-N distance of 2.051 Å.

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Introduction.

A number of ruthenium carbonyl porphyrins have been characterized with respect to their redox properties in non-aqueous media [1]. The one-electron reduction of various (P)Ru(CO) and (P)Ru(CO)(L) complexes where P = the dianion of a given porphyrin ring has been shown to occur at the porphyrin π ring system [1-4], and this was studied in great detail for (TPP)Ru(CO) and (TPP)Ru(CO)(L) where TPP = the dianion of tetraphenylporphyrin and L = a nitrogeneous base or solvent molecule [5].

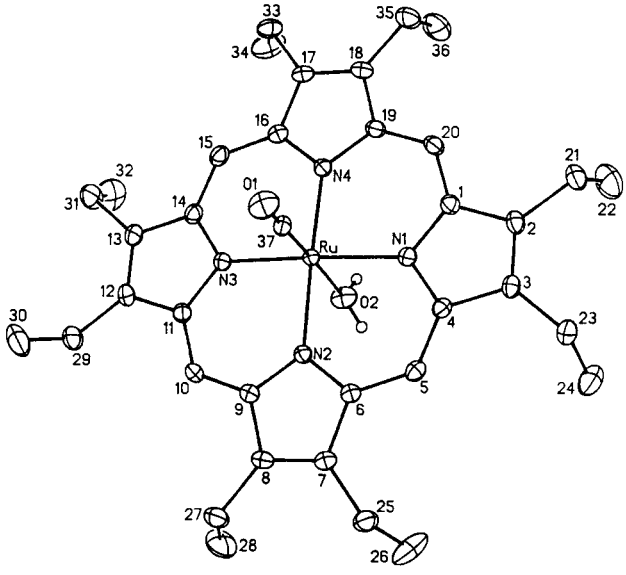

Figure 1. Molecular structure of (OEP)Ru(CO)(H_2O), with non-water hydrogens omitted for clarity.

The generation of a Ru(II) porphyrin π anion radical was thought to invariably result after a one-electron reduction of all Ru(II) carbonyl porphyrins [1], but this is not the case as was recently demonstrated for (OEP)Ru(CO)(L) where OEP = the dianion of octaethylporphyrin and L is one of several different axial ligands [6,7]. These complexes undergo a single one-electron reduction and give as a product either the expected Ru(II) porphyrin π anion radical or a Ru(I) complex depending upon the solvent and/or the specific sixth axial ligand. A π anion radical is generated from (OEP)Ru(CO)(L) in tetrahydrofuran when L is pyridine or DMSO but a Ru(I) porphyrin is the final one-electron reduction product when H_2O or CH_3OH is the sixth axial ligand [7].

Several monomeric Ru(II) [8-11] and Ru(III) [12,13] porphyrins, bimetallic μ-oxo-Ru(IV) porphyrins [14-16] and a Ru(II) metal-metal bonded porphyrin dimer [14] have been characterized by X-ray structural analysis. Two different six-coordinate ruthenium(II) carbonyl tetraphenylporphyrins have also been structurally characterized [17,18], as has been (TDCPP)Ru(CO) (styreneoxide) where TDCPP = tetra-(2,6-dichlorophenyl) porphyrin [19]. However, the structure of an (OEP)Ru(CO)(L) complex has never been

Table 1

Data Collection and Processing Parameters

Chem formula	$C_{37}H_{46}N_4O_2Ru$
fw	679.94
a, Å	10.212 (2)
b, Å	13.717 (4)
c, Å	13.984 (3)
α, deg	114.72(2)
β, deg	104.58 (2)
γ, deg	90.15 (2)
V, Å^3	1709
Z	2
space group	$P\bar{1}$, triclinic
T, °C	17
ρ(calc),g/cm^{-3}	1.32
μ, cm^{-1}	4.84
λ(Mo Kα), Å	0.71073
R, R_W	0.030, 0.034

reported, and it was therefore not known if the different sites of electron addition to (OEP)Ru(CO)(H_2O) and (TPP)Ru(CO)(L) might be related to structural differences between the two types of porphyrin macrocycles. This is investigated in the present paper which presents an X-ray crystal and molecular structure of (OEP)Ru(CO)(H_2O). This is the first structure of a six-coordinate ruthenium(II) carbonyl complex with an octaethylporphyrin (OEP) ring and data for this compound are compared to those for other six-coordinate Ru(II) porphyrin derivatives.

Results and Discussion.

The molecular structure of (OEP)Ru(CO)(H_2O) is presented in Figure 1. Final cell constants, as well as other information pertinent to data collection and refinement are listed in Table I. Tables II and III list the final atomic positional parameters, while Tables IV and V give selected bond distances and angles, respectively.

As can be seen in Figure 1, the environment about the central ruthenium atom is that of an axially distorted octahedron. The four equivalent Ru-N distances average 2.051

Table II
Atomic Coordinates (x10^4) and Their Estimated Standard Deviations

Atom	x	y	z
Ru	1230(1)	3488(1)	3092(1)
O1	3241(3)	3157(2)	1844(2)
O2	-246(3)	3826(2)	4116(2)
N1	2538(3)	3198(2)	4293(2)
N2	1865(3)	5112(2)	3975(2)
N3	-253(3)	3800(2)	1993(2)
N4	431(3)	1890(2)	2315(2)
C1	2710(3)	2211(3)	4301(3)
C2	3800(4)	2350(3)	5265(3)
C3	4266(3)	3416(3)	5817(3)
C4	3474(3)	3951(3)	5204(3)
C5	3634(3)	5041(3)	5485(3)
C6	2892(3)	5595(3)	4937(3)
C7	3044(3)	6755(3)	5294(3)
C8	2101(3)	6953(3)	4542(3)
C9	1362(3)	5921(3)	3710(3)
C10	290(3)	5758(3)	2799(3)
C11	-459(3)	4795(3)	2008(3)
C12	-1586(4)	4660(3)	1066(3)
C13	-2016(4)	3586(3)	493(3)
C14	-1184(3)	3047(3)	1082(3)
C15	-1321(4)	1947(3)	794(3)
C16	-600(4)	1406(3)	1356(3)
C17	-812(4)	254(3)	1036(3)
C18	109(4)	56(3)	1796(3)
C19	901(4)	1083(3)	2598(3)
C20	1961(4)	1241(3)	3509(3)
C21	4275(4)	1455(3)	5563(3)
C22	3454(6)	1190(4)	6197(4)
C23	5351(4)	3990(3)	6875(3)
C24	4769(5)	4552(4)	7839(3)
C25	4036(4)	7549(3)	6329(3)
C26	3525(5)	7826(4)	7334(3)
C27	1804(4)	8027(3)	4556(3)
C28	631(5)	8454(4)	5036(4)
C29	-2132(4)	5567(3)	810(3)
C30	-1405(5)	5861(4)	119(4)
C31	-3159(4)	3016(3)	-552(3)
C32	-4453(5)	2752(5)	-359(4)
C33	-1871(4)	-539(3)	49(3)
C34	-3278(4)	-541(4)	194(4)
C35	279(4)	-1014(3)	1844(3)
C36	-684(6)	-1270(4)	2380(4)
C37	2439(3)	3281(3)	2320(3)

Table III
Hydrogen Atomic Coordinates (x10^4)

Atom	x	y	z
H5	4343	5472	6138
H10	40	6395	2708
H15	-1999	1508	122
H20	2205	605	3604
H21A	4218	818	4900
H21B	5207	1666	6001
H22A	3810	614	6362
H22B	2520	970	5767
H22C	3510	1818	6867
H23A	5910	3472	7005
H23B	5899	4522	6817
H24A	5501	4908	8498
H24B	4224	4027	7909
H24C	4214	5076	7720
H25A	4877	7245	6432
H25B	4194	8201	6255
H26A	4195	8335	7973
H26B	3371	7180	7420
H26C	2688	8137	7244
H27A	2606	8539	4987
H27B	1577	7952	3817
H28A	483	9141	5026
H28B	848	8538	5777
H28C	-181	7952	4607
H29A	-3081	5356	418
H29B	-2035	6196	1489
H30A	-1801	6442	-14
H30B	-1501	5243	-568
H30C	-455	6083	504
H31A	-2878	2355	-1009
H31B	-3323	3475	-921
H32A	-5138	2393	-1048
H32B	-4752	3406	93
H32C	-4307	2286	4
H33A	-1900	-366	-553
H33B	-1607	-1250	-118
H34A	-3899	-1066	-468
H34B	-3564	163	354
H34C	-3271	-721	788
H35A	1197	-990	2254
H35B	111	-1573	1111
H36A	-545	-1955	2395
H36B	-1606	-1300	1973
H36C	-520	-717	3116
H2A	-701	3403	4127
H2B	-29	4260	4693

Å. This is essentially the same as is observed in (TPP)Ru(CO)(py) [2.052 (9) Å] [18], (TPP)Ru(CO)(EtOH) [2.049 (2) Å] [17] and (TDCPP)Ru(CO)(styrene oxide) [2.050 Å] [19] and falls within the range reported for other types of ruthenium porphyrins [9,10]. All of the bond distances and angles of the OEP macrocycle are within the expected range [10,11].

Table IV
Selected Bond Distances (Å)

Ru-N1	2.049(3)	Ru-N2	2.048(3)
Ru-N3	2.054(3)	Ru-N4	2.051(3)
Ru-C37	1.785(4)	Ru-O2	2.253(2)
O1-C37	1.150(4)		

Table V
Selected Bond Angles (deg)

N2-Ru-N1	90.0(1)	N3-Ru-N1	173.0(1)
N3-Ru-N2	89.8(1)	N4-Ru-N1	89.5(1)
N4-Ru-N2	173.2(1)	N4-Ru-N3	89.8(1)
C37-Ru-N1	92.9(1)	C37-Ru-N2	93.6(1)
C37-Ru-N3	94.1(1)	C37-Ru-N4	93.3(1)
O2-Ru-N1	86.6(1)	O2-Ru-N2	83.9(1)
O2-Ru-N3	86.4(1)	O2-Ru-N4	89.3(1)
O2-Ru-C37	177.4(1)	O1-C37-Ru	178.5(3)

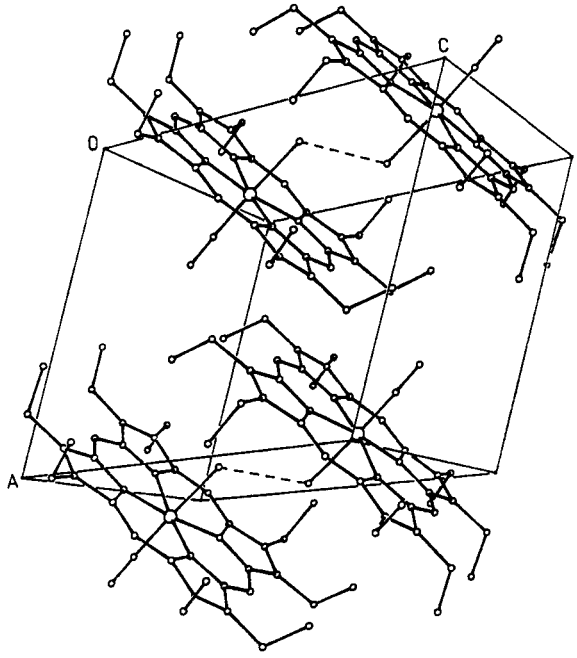

Figure 2. Packing diagram of (OEP)Ru(CO)(H_2O), with hydrogens omitted for clarity. Hydrogen bonds are indicated by dashed lines.

The CO ligand in (OEP)Ru(CO)(H_2O) shows a typically linear Ru-C=O arrangements with a bond angle of 178.5°. This value compares well with CO bond angles in (TDCPP)Ru(CO)(styrene oxide) [177.1°] [19], (TPP)Ru(CO)(EtOH) [175.8°] [17] and (TPP)Ru(CO)(py) [178.4°] [18]. The Ru-CO bond distance of 1.785 (4) Å is shorter than the distance in (TPP)Ru(CO)(py) [1.838 (9) Å] [18] and (TDCPP)Ru(CO)(styrene oxide) [1.811 Å] [19] but slightly longer than the 1.77 (2) Å Ru-CO distance in (TPP)Ru(CO)(EtOH) [17].

The axial water molecules on adjacent complexes are hydrogen bonded through their disordered hydrogens as illustrated in Figure 2. The O-O separation is 3.07 Å. The Ru-O bond distance is 2.253 (2) Å in (OEP)Ru(CO)(H_2O) and this value is slightly longer than the 2.21 (2) Å Ru-O distance in (TPP)Ru(CO)(EtOH) [17]. The long Ru-O bond length in the present complex suggests a possible kinetic lability of the H_2O ligand.

It is noteworthy to point out that the ruthenium atom of (OEP)Ru(CO)(H_2O) is out of the porphyrin plane by 0.14 Å towards CO, thus suggesting the presence of a strong π-π interaction between the metal center and CO. This is also consistent with a weak axial ligand binding of the H_2O molecule [17]. The 0.14 Å metal out-of-plane distance in (OEP)Ru(CO)(H_2O) is much greater than in (TPP)Ru(CO)(py) [18] or (TDCPP)Ru(CO)(styrene oxide) [19] where the ruthenium atom is displaced from the porphyrin plane towards CO by 0.079 Å and 0.11 Å, respectively.

The above data indicate that all of the investigated Ru(II) carbonyl porphyrins have a strong linear CO binding and also that the binding of the sixth axial ligand is relatively weak. Axial ligand binding to the (OEP)Ru(CO) complexes should also be weaker than to the (TPP)Ru(CO) derivatives and this may be accounted for by the fact that the eight ethyl groups on the OEP ring provide more electron density to the cental ruthenium ion which makes π-back bonding from the axial ligand weaker. However, no significant structural differences are observed between the OEP and TPP complexes and it thus appears that structural properties of the neutral Ru(II) porphyrins cannot alone account for the different sites of electron transfer in (OEP)Ru(CO)(H_2O) and (TPP)Ru(CO)(L).

EXPERIMENTAL

Single crystals of (OEP)Ru(CO)(H_2O) suitable for X-ray diffraction were prepared by recrystallization from toluene using a slow room temperature open air evaporation of the solvent. The crystal growth process was carried out in the dark. A large, ruby red prismatic column having approximate dimensions 0.56 x 0.26 x 0.18 mm was mounted on a glass fiber in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either P1 or P$\bar{1}$. Intensities were

measured using the ω-scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every 2 hours or every 100 data collected, and these showed no significant decay. During data reduction Lorentz and polarization corrections were applied, but no correction for absorption was made due to the small absorption coefficient.

The structure was solved by interpretation of the Patterson map, which yielded the position of the Ru atom in space group $P\bar{1}$. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. The water hydrogens were difficult to locate and did not refine well, so the water molecule was treated as a rigid body using an ideal H-O-H angle and O-H distances found in the difference map. Presumably there is some disorder in the water hydrogen locations, since analysis of the crystal packing shows that the molecules group together in pairs across inversion centers such that their axial water molecules are hydrogen bonded. Only one hydrogen would be expected to reside between any given pair of oxygens, and this cannot be accommodated about an inversion center without necessarily implying disorder. Due to the small amount of electron density involved, no attempt was made to introduce a disordered model at this site. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table I. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least squares refinement, and the final difference density map showed a maximum peak of about 0.6 e/Å^3. All calculations were made by using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

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REFERENCES AND NOTES

[1] See K. M. Kadish, *Prog. Inorg. Chem.*, **34**, 435 (1986) and references therein.

[2] D. P. Rillema, J. K. Nagle, L. F. Barringer, Jr. and T. J. Meyer, *J. Am. Chem. Soc.*, **103**, 56 (1981).

[3] K. M. Kadish and D. Chang, *Inorg. Chem..*, **21**, 3614 (1982).

[4] T. Malinski, D. Chang, L. A. Bottomley and K. M. Kadish, *Inorg. Chem.*, **21**, 4248 (1982).

[5] X. H. Mu and K. M. Kadish, *Langmuir*, **6**, 51 (1990).

[6] K. M. Kadish and X. H. Mu, *Pure Appl. Chem.*, **62**, 1051 (1990).

[7] K. M. Kadish, P. Tagliatesta, Y. Hu, Y. J. Deng, X. H. Mu and L. Y. Bao, *Inorg. Chem.*, **30**, 3737 (1991).

[8] R. G. Ball, G. Domazetis, D. Dolphin, B. R. James and J. Trotter, *Inorg. Chem.*, **20**, 1556 (1981).

[9] F. R. Hopf, T. P. O'Brien, W. R. Scheidt and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 277 (1975).

[10] B. R. James, A. Pacheco, S. J. Rettig and J. A. Ibers, *Inorg. Chem.*, **27**, 2414 (1988).

[11] S. Ariel, D. Dolphin, G. Domazetis, B. R. James, T. W. Leung, S. J. Rettig, J. Trotter and G. M. Williams, *Can. J. Chem.*, **62**, 755 (1984).

[12] M. Ke, S. J. Rettig, B. R. James and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 1110 (1987).

[13] B. R. James, D. Dolphin, T. W. Leung, F. W. B. Einstein and A. C. Willis, *Can. J. Chem.*, **62**, 1238 (1984).

[14] J. P. Collman, C. E. Barnes, P. N. Swepston and J. A. Ibers, *J. Am. Chem. Soc.*, **106**, 3500 (1984).

[15] H. Masuda, T. Taga, K. Osaki, H. Sugimoto, M. Mori and H. Ogoshi, *J. Am. Chem. Soc.*, **103**, 2199 (1981).

[17] J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 2141 (1973).

[18] R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 8583 (1973).

[19] J. T. Groves, Y. Han and D. V. Engen, *J. Chem. Soc., Chem. Commun.*, 436 (1990).