5338 *Inorg. Chem.* **1993**, *32*, 5338–5342

Preparation and Structures of Two Sterically Protected Ruthenium Porphyrin Compounds of the Type $Ru(Por)(H_2O)_{in}(CO)_{out}$

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Received July 30, 1993[●]

Two sterically protected ruthenium porphyrin compounds of the type $Ru(Por)(H_2O)_{in}(CO)_{out}$ have been prepared, and their structures have been determined by single-crystal X-ray diffraction methods. Both compounds, $Ru(\beta\text{-PocPivP})(H_2O)_{in}(CO)_{out}$ (**1**), a "pocket" porphyrin, and $Ru(OCCOPor)(H_2O)_{in}(CO)_{out}$ (**2**), a "capped" porphyrin, pack as discrete porphyrin units with solvate molecules. In both compounds, the H_2O ligand is inside the sterically protected region while the CO ligand is trans to the H_2O molecule and is on the outside of the protected region. In $Ru(\beta\text{-PocPivP})(H_2O)_{in}(CO)_{out}$, the H_2O ligand is hydrogen-bonded to an amide oxygen atom, the $O(H_2O)$–O(amide) distance being 2.688(4) Å; in $Ru(OCCOPor)(H_2O)_{in}(CO)_{out}$, the H_2O ligand, though not involved in traditional hydrogen bonding, may interact with the aromatic π system of the benzene cap, the $O(H_2O)$–cap centroid distance being 2.98 Å. The carbonyl groups have their normal, linear arrangement, with the Ru–C–O angles being 178.7(3) and 178.1(4)° in **1** and **2**, respectively. In each structure, the porphyrin plane is slightly ruffled, with the Ru atom lying 0.20 and 0.26 Å below the porphyrin plane toward the carbonyl group in **1** and **2**, respectively. In each structure, the cap is off-center and tilted. Each cap centroid lies 4.25 (**1**) and 4.79 Å (**2**) above the porphyrin plane. These structures provide some useful insights into steric constraints in these encumbered porphyrins. Crystallographic data for $Ru(\beta\text{-PocPivP})(H_2O)_{in}(CO)_{out}\cdot 2CHCl_3$ (**1**): triclinic, C_i^1-$P\bar{1}$, $Z = 2$, $a = 13.261(3)$ Å, $b = 14.450(3)$ Å, $c = 15.716(3)$ Å, $\alpha = 91.63(3)°$, $\beta = 94.94(3)°$, $\gamma = 94.40(3)°$, $t = -167$ °C, 11 611 unique reflections, 805 variables, $R(F)$ $(F_o^2 > 2\sigma(F_o^2)) = 0.045$, $R_w(F^2) = 0.101$. Crystallographic data for $Ru(OCCOPor)(H_2O)_{in}(CO)_{out}\cdot 2CHCl_3\cdot {}^1/_2 n\text{-}C_6H_{12}$ (**2**): triclinic C_i^1-$P\bar{1}$, $Z = 2$, $a = 9.651(2)$ Å, $b = 11.936(2)$ Å, $c = 25.964(5)$ Å, $\alpha = 92.14(3)°$, $\beta = 91.58(3)°$, $\gamma = 104.99(3)°$, $t = -167$ °C, 15 970 unique reflections, 760 variables, $R(F)$ $(F_o^2 > 2\sigma(F_o^2)) = 0.086$, $R_w(F^2) = 0.183$.

Introduction

The binding of small molecules to porphyrins that model the heme active site has been of considerable interest over the past quarter century. The assessment of steric interactions and their effect on the binding of small molecules, such as O_2, CO, and RNC, has provided considerable insight into structure–function relationships in heme systems.[1–10] Some of these models have employed Ru, rather than Fe, because the resultant Ru complexes are often more robust and are low spin.[11–26] A few structures of heme models with a small molecule or ligand bound on the inside of a sterically hindered region, as in the ligated hemes, have been reported. These include structures with O_2,[27,28] CO,[29–32] and CN^-.[33] Here we report the synthesis and structures of two compounds of the type $Ru(Por)(H_2O)_{in}(CO)_{out}$, where Por = PocPivP[31,34,35]

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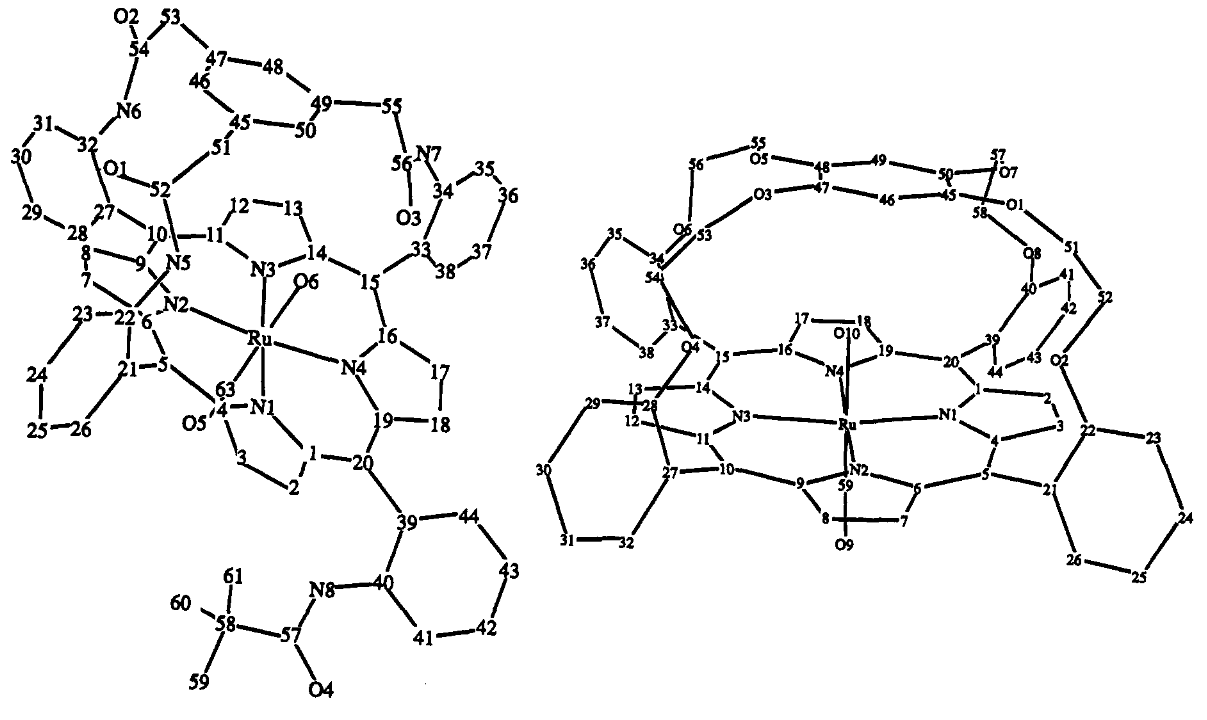
[●] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Morgan, B.; Dolphin, D. *Struct. Bonding (Berlin)* **1987**, *64*, 115–203.
(2) Xavier, A. V., Ed. *Frontiers in Bioinorganic Chemistry*; VCH: Weinheim, Germany, 1986.
(3) Lopez, M. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 6212–6222.
(4) Proniewicz, L. M.; Bruha, A.; Nakamoto, K.; Kyuno, E.; Kincaid, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 7050–7056.
(5) Gerothanassis, I. P.; Momenteau, M.; Loock, B. *J. Am. Chem. Soc.* **1989**, *111*, 7006–7012.
(6) Baltzer, L.; Landergren, M. *J. Am. Chem. Soc.* **1990**, *112*, 2804–2805.
(7) Perutz, M. F.; Fermi, G.; Luisi, B.; Shaanan, B.; Liddington, R. C. *Acc. Chem. Res.* **1987**, *20*, 309–321.
(8) Garcia, B.; Lee, C.-H.; Blaskó, A.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 8118–8126.
(9) Schnatter, W. F. K.; Almarsson, Ö.; Bruice, T. C. *Tetrahedron* **1991**, *47*, 8687–8700.
(10) Zhang, H.-Y.; Blaskó, A.; Yu, J.-Q.; Bruice, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 6621–6630.
(11) Seyler, J. W.; Fanwick, P. E.; Leidner, C. R. *Inorg. Chem.* **1990**, *29*, 2021–2023.
(12) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3486–3495.
(13) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3477–3486.
(14) Paulson, D. R.; Bhakta, S. B.; Hyun, R. Y.; Yuen, M.; Beaird, C. E.; Lee, S. C.; Kim, I.; Ybarra, J., Jr. *Inorg. Chim. Acta* **1988**, *151*, 149–152.
(15) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500–3510.
(16) Corsini, A.; Chan, A.; Mehdi, H. *Talanta* **1984**, *31*, 33–38.
(17) Pomposo, F.; Carruthers, D.; Stynes, D. V. *Inorg. Chem.* **1982**, *21*, 4245–4248.
(18) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *J. Am. Chem. Soc.* **1981**, *103*, 2199–2203.
(19) Paulson, D. R.; Addison, A. W.; Dolphin, D.; James, B. R. *J. Biol. Chem.* **1979**, *254*, 7002–7006.
(20) Hopf, F. R.; O'Brien, T. P.; Scheidt, W. R.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 277–281.
(21) Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 235–236.
(22) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151–5163.
(23) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141–2149.
(24) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 8583–8590.
(25) Tsutsui, M.; Ostfeld, D.; Francis, J. N.; Hoffman, L. M. *J. Coord. Chem.* **1971**, *1*, 115–119.
(26) Tsutsui, M.; Ostfeld, D.; Hoffman, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 1820–1823.
(27) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 3224–3237.
(28) Jameson, G. B.; Rodley, G. A.; Robinson, W. T.; Gagne, R. R.; Reed, C. A.; Collman, J. P. *Inorg. Chem.* **1978**, *17*, 850–857.
(29) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. C.; Christoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5919–5923.
(30) Ricard, L.; Weiss, R.; Momenteau, M. *J. Chem. Soc., Chem. Commun.* **1986**, 818–820.
(31) Kim, K.; Fettinger, J.; Sessler, J. L.; Cyr, M.; Hugdahl, J.; Collman, J. P.; Ibers, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 403–405.
(32) Kim, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6077–6081.
(33) Schappacher, M.; Fisher, J.; Weiss, R. *Inorg. Chem.* **1989**, *28*, 389–390.
(34) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B. L.; Lang, G.; Pettman, R. B.; Sessler, J. L.; Walters, M. A. *J. Am. Chem. Soc.* **1983**, *105*, 3038–3052.

0020-1669/93/1332-5338\$04.00/0



1

2

Figure 1. Labeling schemes for $Ru(\beta\text{-PocPivP})(H_2O)_{in}(CO)_{out}$ (**1**) and $Ru(OCCOPor)(H_2O)_{in}(CO)_{out}$ (**2**).

or OCCOPor[36] (Figure 1). These structures provide some useful insights into steric constraints in these encumbered porphyrins.

Experimental Section

UV/vis spectra were obtained either on a Perkin-Elmer 330 spectrometer or a Hewlett Packard 8952A diode array spectrometer. ^1H NMR spectra were recorded on a Varian XL-400 spectrometer or a Gemini 300 spectrometer. IR spectra were obtained on a Perkin-Elmer 283 infrared spectrometer or a Nicolet 520SX infrared spectrometer. Mass spectra data were obtained by the LSIM technique either at the Mass Spectrometry Facility, University of California, San Francisco, or at the Analytical Services Laboratory of Northwestern University. The free-base porphyrin $H_2(\alpha\text{-PocPivP})$ was kindly supplied by Prof. J. P. Collman. All solvents and reagents were used as purchased except for 2-methoxyethanol, which was dried over 4-Å molecular sieves, and 4-picoline, which was passed through a short alumina column prior to use.

Ruthenium Insertion into $H_2(\alpha\text{-PocPivP})$. To boiling 2-methoxyethanol (50 mL) were added $H_2(\alpha\text{-PocPivP})$ (54 mg, 0.056 mmol) and $Ru_3(CO)_{12}$ (110 mg, 0.17 mmol), and the reaction mixture was heated at reflux for 2 days under N_2. The solvent was removed under reduced pressure, and the residue was flash-chromatographed (silica gel, 5 × 20 cm) with dichloromethane as the eluent. Two closely spaced orange bands were resolved by eluting with a 1:1 mixture of dichloromethane and diethyl ether. The two bands were collected separately and evaporated to dryness. Yields of the first eluted material (band 1) and the second material (band 2) were 18 and 20 mg, respectively. The UV/vis spectra of both band 1 and band 2 are essentially identical (λ_{max} 412, 544 nm) and similar to that of Ru(TPP)(CO)(MeOH).[37] Although band 1 is a single product, band 2 is a mixture of two compounds, as indicated by ^1H NMR spectroscopy.

$Ru(\beta\text{-PocPivP})(H_2O)_{in}(CO)_{out}\cdot 2CHCl_3$. The band 2 material (5 mg) was dissolved in 3 mL of chloroform, and two drops of 4-picoline were added. The solution was transferred to several diffusion tubes, and *n*-hexane was allowed to diffuse into the solutions at room temperature. Crystals suitable for X-ray work were obtained in a month: UV/vis λ_{max} 412, 544, 595 nm (sh); IR (Nujol) ν(CO) 1934 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (9H, s, t-Bu), 1.96 (2H, d, J = 15 Hz, methylene bridges), 2.53 (2H, d, J = 15 Hz, methylene bridges), 3.36 (2H, s, methylene bridges), 3.50 (1H, s, triacetylphenyl) 4.93 (1H, s, amide NH), 5.79 (2H, s, triacetylphenyl), 6.14 (2H, s, amide NH), 6.66 (1H, s, amide NH), 7.31–8.93 (24H, m, aromatic and pyrrolic CH); HRMS calcd for $C_{62}H_{46}N_8O_5Ru$ (parent peak − H_2O) m/z 1086.2645, found m/z 1086.2810.

Ruthenium Insertion into H_2(OCCOPor). In the absence of light, a benzene solution (15 mL) containing H_2(OCCOPor)[36] (50 mg, 0.047 mmol) and $Ru_3(CO)_{12}$ (103 mg, 0.16 mmol) was refluxed for 3 days under Ar.[26,38] The solvent was removed under vacuum, and the residue was purified on a preparative, centrifugally accelerated, thin-layer chromatograph (chromatotron). In minimal light, the reaction residue was loaded onto a 1-mm silica (Aldrich TLC grade with gypsum binder) rotor and eluted with 40% hexanes/60% chloroform. A bright orange band was collected and evaporated to dryness: yield 34 mg (58%); UV/vis (THF) λ_{max} (log ϵ) 412 (5.08), 528 (4.08), 552 nm (3.40); IR (KBr) ν(CO) 1927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.52 (4H, m, $C_6H_2(OCH_2CH_2O)_4$–porph), 2.75 (4H, m, $C_6H_2(OCH_2CH_2O)_4$–porph), 3.49 (2H, s, benzene cap), 3.72 (4H, m, $C_6H_2(OCH_2CH_2O)_4$–porph), 3.91 (4H, m, $C_6H_2(OCH_2CH_2O)_4$–porph), 7.40 (4H, d, *meso* phenyl 3-proton), δ 7.52 (4H, t, *meso* phenyl 4-proton), δ 7.78 (4H, t, *meso* phenyl 5-proton), δ 8.25 (4H, d, *meso* phenyl 6-proton), δ 8.65 (8H, pyrrolic CH); MS calcd for $C_{59}H_{42}N_4O_9Ru$ (parent peak − H_2O) m/z 1052, found m/z 1052.

$Ru(OCCOPor)(H_2O)_{in}(CO)_{out}\cdot 2CHCl_3\cdot {}^1/_2n\text{-hexane}$. Approximately 3 mg of the above product was dissolved in $CHCl_3$ (1 mL). The solution was transferred to a diffusion tube, and *n*-hexane was allowed to diffuse into the solution at 4 °C. Red-orange crystals suitable for X-ray diffraction were obtained in 2 weeks.

X-ray Crystal Structure Determination of $Ru(\beta\text{-PocPivP})(H_2O)_{in}(CO)_{out}\cdot 2CHCl_3$ (1). To prevent solvent evaporation, the chosen crystal was coated with paratone-N oil and mounted quickly in the cold stream (−167 °C) of an Enraf Nonius CAD4 diffractometer. Unit cell parameters were determined by least-squares refinement of 25 reflections that had been automatically centered on the diffractometer. Intensity data were collected, processed, and corrected for absorption.[39] Crystallographic details are given in Table I. Cell reduction did not suggest higher symmetry; the triclinic space group C_i^1-$P\bar{1}$ was therefore assigned. With

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(35) Collman, J. P.; Brauman, J. I.; Collins, T. J.; Iverson, B.; Sessler, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 2450–2452.

(36) Johnson, M. R.; Seok, W. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 3998–4000.

(37) Abbreviations: TPP = tetraphenylporphyrinato dianion; 1,2-Me_2Im = 1,2-dimethylimidazole; 1-MeIm = 1-methylimidazole.

(38) Cullen, D.; Jun, E. M.; Srivastava, T. S.; Tsutsui, M. *J. Chem. Soc., Chem. Commun.* **1972**, 584–585.

(39) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

Table I. Selected Crystallographic Data

compd	Ru(β-PocPivP)$(H_2O)_{in}(CO)_{out}$ (**1**)	Ru(OCCOPor)$(H_2O)_{in}(CO)_{out}$ (**2**)
chem formula	$C_{62}H_{48}N_8O_6Ru\cdot 2CHCl_3$	$C_{59}H_{44}N_4O_{10}Ru\cdot 2CHCl_3\cdot {}^1/_2C_6H_{14}$
fw	1340.89	1351.87
space group	$C_i^1 - P\bar{1}$	$C_i^1 - P\bar{1}$
a, Å	13.261(3)	9.651(2)
b, Å	14.450(3)	11.936(2)
c, Å	15.716(3)	25.964(5)
α, deg	91.63(3)	92.14(3)
β, deg	94.94(3)	91.58(3)
γ, deg	94.40(3)	104.99(3)
V, Å^3	2989.6(11)	2885.0(9)
Z	2	2
temp, °C	−167	−167
density, g/cm^3	1.490	1.556
radiation (λ, Å)	Mo Kα_1 (0.7093)	Mo Kα_1 (0.7093)
μ, cm^{-1}	5.84	6.09
transm factor	0.863–0.941	0.876–0.935
$R(F)$ $(F_o^2 > 2\sigma(F_o^2))$	0.0445	0.0855
$R_w(F^2)$	0.101	0.183

Table II. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	1	**2**
Ru–N(1)	2.032(3)	2.055(4)
Ru–N(2)	2.033(3)	2.056(4)
Ru–N(3)	2.040(3)	2.059(4)
Ru–N(4)	2.031(3)	2.047(4)
av Ru–N	2.034(4)	2.054(5)
Ru–C(CO)	1.813(3)	1.794(5)
Ru–O(H_2O)	2.198(2)	2.187(4)
C(CO)–O(CO)	1.149(4)	1.157(6)
av N–C_a	1.369(5)	1.374(7)
av C_a–C_b	1.443(6)	1.438(7)
av C_b–C_b	1.346(3)	1.354(7)
av C_a–C_m	1.401(7)	1.400(7)
Ru–C–O(CO)	178.7(3)	178.1(4)
C(CO)–Ru–N(1)	94.68(12)	93.1(2)
C(CO)–Ru–N(2)	94.50(12)	95.5(2)
C(CO)–Ru–N(3)	91.76(12)	95.7(2)
C(CO)–Ru–N(4)	92.77(12)	92.2(2)
C(CO)–Ru–O(H_2O)	178.91(12)	179.5(2)
O(H_2O)–Ru–N(1)	84.28(9)	86.9(2)
O(H_2O)–Ru–N(2)	85.83(9)	84.0(2)
O(H_2O)–Ru–N(3)	89.29(9)	84.3(2)
O(H_2O)–Ru–N(4)	86.91(9)	88.3(2)
N(1)–Ru–N(2)	90.32(10)	89.3(2)
N(1)–Ru–N(3)	173.55(9)	171.2(2)
N(1)–Ru–N(4)	89.81(10)	89.8(2)
N(2)–Ru–N(3)	88.76(10)	90.5(2)
N(2)–Ru–N(4)	172.70(9)	172.3(2)
N(3)–Ru–N(4)	90.29(10)	89.2(2)

the use of the direct methods program SHELXS,[40] a solution was found in this space group. Standard procedures and programs were used to develop the structure. The final refinement[41] on F^2 involved an anisotropic model for all non-hydrogen atoms and fixed positions for the hydrogen atoms. The hydrogen atoms of the water molecule were previously located in a difference electron density map, but their positions were not refined. There were 11 611 independent observations and 805 variables. This refinement converged to the *R* indices given in Table I. The atom-labeling scheme is given in Figure 1. Table II provides selected metrical data. Additional crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, additional bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters are available in Tables SI–SV.[42] The program package SHELXTL PC[40] was used for the ensuing molecular graphics generation.

X-ray Crystal Structure Determination of Ru(OCCOPor)$(H_2O)_{in}(CO)_{out}\cdot 2CHCl_3\cdot {}^1/_2n\text{-}C_6H_{12}$ (2). The same procedures for data collection and reduction, for structure development and refinement, and for graphics generation were employed. The final refinement on F^2 involved an anisotropic model for all non-hydrogen atoms, with the exception of a badly disordered hexane solvent molecule. Ten isotropic pseudoatoms were generated, and the disordered solvent was represented as their sum. The occupancies of these pseudoatoms were refined.[41] This final refinement of 760 variables and 15 972 observations converged to the *R* indices given in Table I. The atom-labeling scheme for Ru(OCCOPor)$(H_2O)_{in}(CO)_{out}$ is given in Figure 1. Selected metrical data are given in Table II. Additional crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, additional bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters are available in Tables SVII–SXI.[42]

Results and Discussion

Syntheses. The insertion of Ru into H_2(α-PocPivP) by reaction of the porphyrin with $Ru_3(CO)_{12}$ in refluxing (124 °C) 2-methoxyethanol, followed by solvent removal and flash chromatography, conceivably could afford six distinct compounds (Chart I), namely Ru(α/β-PocPivP)$(H_2O)_{in}(CO)_{out}$ and Ru(α/β-PocPivP)$L_{out}(CO)_{in}$, where α-PocPivP is the isomer with the pivaloyl group on the cap side of the porphyrin (**A**, **B**) and β-PocPivP is the isomer with the pivaloyl group on the side opposite from the cap (**C**, **D**) and where L = 2-methoxyethanol or H_2O (introduced during the chromatography). This chromatography afforded two bands with essentially identical UV/vis spectra. Band 1 is a single compound. Subsequent dissolution of the band 1 material in chloroform in the presence of 1-methylimidazole has afforded crystals of Ru(α-PocPivP)$(1\text{-MeIm})_{out}(CO)_{in}$.[43] This suggests that band 1 is Ru(α-PocPivP)$L_{out}(CO)_{in}$ (**A**). On the other hand, band 2 is a mixture of two compounds, as deduced from NMR spectroscopy; no attempt was made to separate these two compounds. Rather, when the mixture was dissolved in chloroform in the presence of 4-picoline, with the original intent of preparing Ru(α-PocPivP)$(CO)_{in}(4\text{-picoline})_{out}$, there resulted Ru($\beta$-PocPivP)$(H_2O)_{in}(CO)_{out}$ (**1**) (**D** in Chart I). The conversion of α-PocPivP to β-PocPivP under harsh metalation conditions has been seen before.[31] The NMR spectrum of this material is identical with the spectrum of one of the components of band 2. The nature of the second component of band 2 remains unknown, although Ru(β-PocPivP)$(H_2O)_{out}(CO)_{in}$ (**C**) and Ru(α-PocPivP)$(H_2O)_{in}(CO)_{out}$ (**B**) seem most likely. Regardless of this second component and the product that it might afford when dissolved in chloroform in the presence of 4-picoline, Ru(β-PocPivP)$(H_2O)_{in}(CO)_{out}$ (**1**), the product actually obtained, must be the least soluble under the crystallization conditions used.

No base was introduced in the attempted preparation of Ru(OCCOPor)(CO). The compound Ru(OCCOPor)$(H_2O)_{in}(CO)_{out}$ resulted, with H_2O probably being introduced during the chromatography or possibly as an impurity in the solvents.

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(40) Sheldrick, G. M. *SHELXTL PC, Version 4.1: An integrated system for solving, refining, and displaying crystal structures from diffraction data*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

(41) Sheldrick, G. M. SHELXL-92, Unix Beta-test Version.

(42) Supplementary material.

(43) Seok, W. K.; Ibers, J. A. Unpublished results.

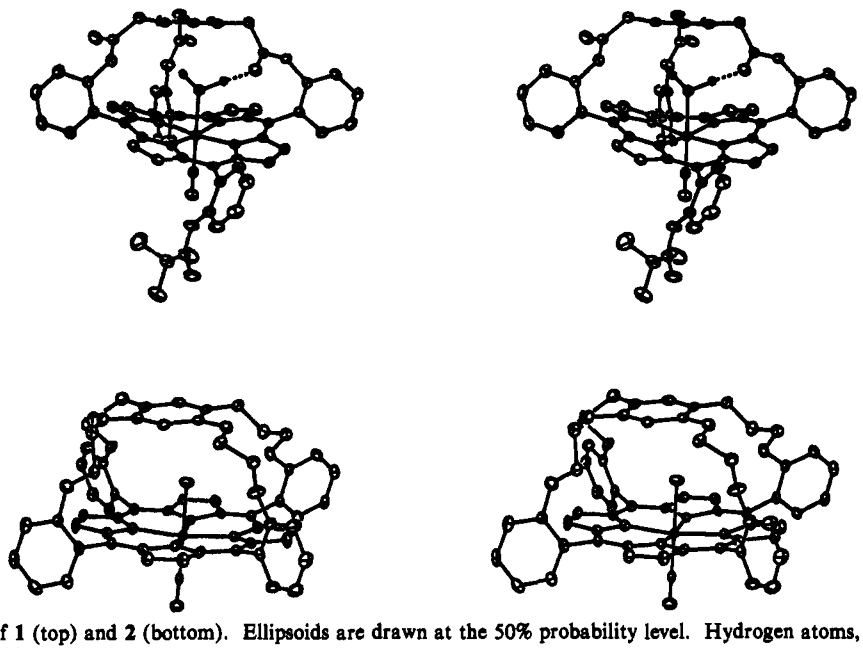
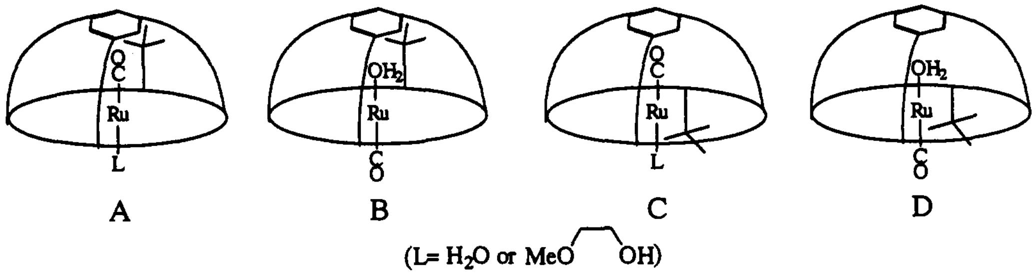


Figure 2. Stereoviews of **1** (top) and **2** (bottom). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for those of the H_2O molecule in **1**, are omitted.

Chart I



Description of the Structures. Each crystal structure consists of the packing of a crystallographically independent porphyrin molecule with solvent molecules. Stereoviews of **1** and **2** are shown in Figure 2. In compound **1**, Ru(β-PocPivP)$(H_2O)_{in}$-$(CO)_{out}$ (Figure 1), the protected area consists of a benzene cap linked at the 1,3,5-positions by three-atom arms ($CH_2(C{=}O)$-NH) that connect to the ortho positions of three of the four phenyl groups of a ruthenium tetraphenylporphyrin. The pivaloyl group, which is connected to the fourth phenyl group, extends away from the cap. Both H_2O and CO are bound to the Ru center; the H_2O molecule is inside this protected area and hydrogen-bonded to an amide O atom of an arm while the CO molecule is outside. To accommodate the H_2O molecule, the phenyl cap is displaced from the porphyrin centroid and is not parallel to the porphyrin plane. In compound **2**, Ru(OCCOPor)$(H_2O)_{in}(CO)_{out}$ (Figure 1), the protected area consists of a benzene cap linked at the 1,2,4,5-positions by four-atom arms (OCH_2CH_2O) that connect to the ruthenium tetraphenylporphyrin. Again H_2O is found inside the protected area, this time not hydrogen-bonded to any atom of an arm, while CO is found outside. Complex **2** exhibits distortions similar to those in complex **1**, but the fourth arm limits the degree to which the cap can move laterally with respect to the porphyrin.

The porphyrin plane of **1** is ruffled with a mean deviation of 0.21 Å and a maximum deviation of 0.48 Å (atom C(10)). The four nitrogen atoms lie slightly below the mean plane (i.e., opposite the cap) with an average deviation of 0.07 Å. The ruthenium atom lies 0.20 Å below the mean plane. The porphyrin plane of **2** is slightly less distorted, with an average deviation of 0.06 Å and a maximum deviation of 0.17 Å (atom N(2)). The four nitrogen atoms lie an average of 0.11 Å below the porphyrin plane, and the ruthenium atom is 0.26 Å below. The average Ru–N bond lengths for **1** and **2** are 2.034(4) and 2.054(5) Å. The Ru–N bond distance in **1** is relatively short compared to those in other known Ru(II) porphyrins.[11-13,15,23,24,44-49] The Ru–C(CO) and C–O distances are 1.813(3) and 1.149(4) Å in **1** and 1.794(5) and 1.157(6) Å in **2**. The Ru–C–O bonds are essentially linear with angles of 178.7(3) and 178.1(4)°, respectively, for **1** and **2**. The Ru–O(H_2O) distances are 2.198(2) and 2.187(4) Å, both within the expected range when compared to other Ru(II)–O bonds in porphyrins. Metrical data for various carbonylated metalloporphyrins are summarized in Table III.

Unlike Fe(β-PocPivP)(1,2-Me_2Im)(CO),[31] the other reported complex of PocPivP, compound **1** has one amide oxygen atom directed inward to afford the hydrogen bond with the H_2O molecule (O(3)–O(6) = 2.688(4) Å). This results in different cap torsion angles and different dihedral angles. The torsion angles for the atoms directly attached to the cap are 91.6° (C(50)–C(49)–C(55)–C(56)), −128.8° (C(50)–C(45)–C(51)–C(52)), and 84.8° (C(48)–C(47)–C(53)–C(54)). Respective torsion angles for Fe(β-PocPivP)(CO)(1,2-Me_2Im) are 128.0, −141.8, and 85.3°. The cap is tilted slightly less for **1** than for Fe(β-PocPivP)(1,2-Me_2Im)(CO), with dihedral angles of 13.8 and 17.6°, respectively, between cap and mean porphyrin plane. While

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(44) Groves, J. T.; Han, Y.; Van Engen, D. *J. Chem. Soc., Chem. Commun.* **1990**, 436–437.

(45) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755–762.

(46) Ball, R. G.; Domazetis, G.; Dolphin, D.; James, B. R.; Trotter, J. *Inorg. Chem.* **1981**, *20*, 1556–1562.

(47) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Inorg. Chem.* **1982**, *21*, 2647–2649.

(48) Seyler, J. W.; Fanwick, P. E.; Leidner, C. R. *Inorg. Chem.* **1992**, *31*, 3699–3700.

(49) James, B. R.; Pacheco, A.; Rettig, S. J.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2414–2421.

Table III. Metrical Data for Selected Carbonylated Metalloporphyrins

	av M–N, Å	M–C(CO), Å	M–C–O, deg	M–L (trans to CO), Å	av dev from 24-atom plane, Å	Ru or Fe dev from 24-atom plane, Å
Ru(TPP)(Py)(CO)[a]	2.052(9)	1.838(9)	178.4(7)	2.193(4)	0.03	0.079[f]
Ru(TPP)(EtOH)(CO)[b]	2.049(5)	1.77(2)	176(2)	2.21(2)	0.02	0[g]
Ru(β-PocPivP)$(H_2O)_{in}(CO)_{out}$[c]	2.034(4)	1.813(3)	178.7(3)	2.198(2)	0.21	0.20
Ru(OCCOPor)$(H_2O)_{in}(CO)_{out}$[c]	2.054(5)	1.794(5)	178.1(4)	2.187(4)	0.06	0.26
Fe(PocPivP)(1,2-MeIm)(CO)[d]	1.973(8)	1.768(7)	172.5(6)	2.079(5)	0.27	0.008
Fe(C_2Cap)(1-MeIm)(CO)[e]						
molecule 1	1.990(7)	1.742(7)	172.9(6)	2.043(6)	0.085	0.019
molecule 2	1.988(13)	1.748(7)	175.9(6)	2.041(5)	0.084	−0.008

[a] Reference 24. [b] Reference 23. [c] This work. [d] Reference 31. [e] Reference 32. [f] Positive value indicates displacement toward the CO group. [g] By symmetry.

the distances from the cap centroids to the porphyrin planes are the same in both compounds (4.23 and 4.25 Å), the horizontal displacement of the centroid of the benzene cap is less in **1** than in the Fe compound (3.0 vs 3.3 Å).

There is some evidence for hydrogen bonding between H_2O and the π system of aromatic rings.[50,51] In **2**, the oxygen atom of the water is 2.98 Å from the centroid of the benzene cap. Although the hydrogen atoms of the water molecule were not located, from geometrical considerations they must be 2.6–3.1 Å from this centroid, in the range of values reported earlier for a hydrogen-bonding interaction.[50]

One can use the present results on **2** in conjunction with earlier structural data on capped porphyrins to estimate the geometrical changes necessary if a CO molecule is to bind to Fe or Ru inside the cap of OCCOPor. In H_2(OCCOPor), the average distance from the cap centroid to the 24-atom porphyrin plane is 3.81 Å and the cap is tilted at a dihedral angle of 8°.[36] In **2**, where the H_2O molecule is accommodated beneath the cap, the cap-to-porphyrin distance increases by 0.99 Å to 4.80 Å and the dihedral angle decreases to 5.1°. In the Fe(C_2Cap)(1-MeIm)$_{out}$(CO)$_{in}$[37,32] molecule the cap-to-porphyrin distance increases about 1.7 Å over that found in H_2(C_2-Cap)[52] and FeCl(C_2-Cap).[53,54] Thus if the OCCOPor system is to accommodate a CO molecule beneath the cap, an expansion of about another 0.7 Å over that found in the present $(H_2O)_{in}$ complex will be necessary. Hence, the OCCOPor system will have to distort significantly more, through further stretching of the arms, tilting of the cap, and displacement of the cap centroid from porphyrin centroid, to accommodate a CO molecule, such expansion being embodied in the energetics of binding. Absorbance measurements indicate that this expansion occurs. Spectra for carbon monoxide binding to Fe(OCCOPor) in 1 M 1-MeIm/toluene are isosbestic and lead to a remarkably high $P_{1/2}$ of 100 Torr[36] at 26 °C compared with values such as 0.0054 Torr for Fe(C_2-Cap)(1-MeIm)[55] and 0.0015 Torr for Fe(PocPivP)(1-MeIm).[35]

Acknowledgment. We thank Dr. M. R. Johnson for his helpful discussions and advice, Prof. J. P. Collman for the gift of H_2(α-PocPivP), and Prof. Chad Mirkin for providing access to a UV/visible spectrometer. This research was kindly supported by U.S. National Institutes of Health (Grant HL13157). C.S. acknowledges partial support as a U.S. Department of Education GANN/DOW Chemical Graduate Fellow.

Supplementary Material Available: Tables SI–SV and SVII–SXI, giving crystallographic data, atomic coordinates and isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **1** and **2**, respectively (23 pages). Ordering information is given on any current masthead page.

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(50) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942–945.

(51) Atwood, J. L.; Hamada, F.; Robinson, K. D.; Orr, G. W.; Vincent, R. L. *Nature* (*London*) **1991**, *349*, 683–684.

(52) Jameson, G. B.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2823–2831.

(53) Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 3715–3721.

(54) The C_2-Cap molecule has five-atom arms ((C=O)OCH$_2$CH$_2$O) extending from the 1,2,4,5 positions of the benzene cap and attached to the ortho positions of the four phenyl groups of tetraphenylporphyrin.

(55) Hashimoto, T.; Dyer, R. L.; Crossley, M. J.; Baldwin, J. E.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 2101–2109.