**Acknowledgment.** This work was supported by Grant 5R01-AP00771-4 from the Environmental Protection Agency, U. S. Public Health Service. H. F. thanks the Deutsche Forschungsgemeinschaft for financial assistance. The authors thank Mr. Jeff Gaffney for his able assistance.

(12) It has been suggested by a referee that $O_2^-$, generated during the aqueous decomposition of potassium perchromate, may be the actual source of singlet oxygen. Although $O_2^-$ is quite probably generated in the $K_3CrO_8$ decomposition, Khan has shown, in the case of potassium superoxide, that if any excited molecular oxygen is formed from $O_2^-$, it is in the $^1\Sigma$ state and is rapidly quenched by water and hence would not be detected in our system.

(13) NOTE ADDED IN PROOF. We have recently detected $O_2$ ($^1\Delta$ spectral emission) from the thermal decomposition of the pure dry potassium perchromate salt which will be described in a forthcoming communication.

**J. W. Peters, J. N. Pitts, Jr.,* I. Rosenthal, H. Fuhr**
*Department of Chemistry, University of California*
*Riverside, California 92502*

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## Metalloporphyrin Photochemistry. A Ruthenium(II) Porphyrin Photodimer with a Metal–Metal Bond

*Sir:*

We wish to report a novel and facile photoreaction of ruthenium(II) porphyrins which apparently involves photochemical ejection of a CO ligand with subsequent formation of a dimer. Whereas complexes containing two metalloporphyrins linked *via* an oxo bridge,[1] two porphyrins bound to one metal,[2] and one porphyrin bound to two metals[3] have been previously prepared, the present reaction is apparently the first case involving formation of a metalloporphyrin dimer linked through a metal–metal bond.

Irradiation of degassed benzene or pyridine solutions of ruthenium(II) carbonyletioporphyrin I pyridinate[4] (**1**) with visible or ultraviolet light leads quantitatively to photoproduct **2a**. The reaction can be followed by changes in the uv–visible spectra (Figure 1) (isosbestic points at 532, 436, 422, 408, and 391 nm) resulting in loss of the characteristic metalloporphyrin spectrum or by loss of the carbonyl stretching frequency at 1931 cm$^{-1}$ in the ir.[5] In a typical "preparative" experiment a suspension of 0.04 g of **1** in 4 ml of pyridine was irradiated with a medium-pressure mercury lamp (Pyrex filter) for 36 hr; formation of crystals of the highly insoluble **2a** was observed as the irradiation progressed. The crystals were recovered by filtration and recrystallized (with difficulty) from pyridine. Irradiation of the octaethylporphyrin analog of **1** under the same conditions led to the octaethylporphyrin derivative **2b** which proved to be easier to purify and generally much more soluble in organic solvents. Elemental analysis shows that **2a** has lost CO and contains pyridine and ruthenium etioporphyrin in a 1:1 ratio. *Anal.* Calcd for $(C_{32}H_{36}N_4Ru)_x \cdot (C_5H_5N)_x$: C, 67.66; H, 6.29; Ru, 15.39; O, 0.0. Found: C, 68.02; H, 6.08; Ru, 14.90; O, 0.13.

Mass spectral analysis reveals that **2a** is a dimer of the starting material. High-resolution spectrometry indicates that the parent ion has a composition[6] of $Ru_2C_{64}H_{72}N_8$; the peaks occur in the clusters expected for the ruthenium isotopes. Little fragmentation is evident except for the usual peaks corresponding to loss of methyl groups; a notable feature of the mass spectrum is the condensed clusters at one-half (spacing every 0.5 mass unit) and one-third the parent ion mass which correspond to doubly and triply charged ions of **2a**. The nmr spectrum of **2b** (Table I) shows only the resonances expected for the three types of porphyrin protons in octaethylporphyrin in the expected ratios, indicating that the porphyrin ring has not been altered.[7] From the nmr spectrum, together with the fact that loss of CO accompanies formation of **2**, it is apparent that the dimer must result *via* metal–metal bonding; since each ruthenium is bound to four porphyrin nitrogens and one pyridine and the complex is diamagnetic,[10] the ruthenium–ruthenium bond is formally a double bond.[11,12]

**Table I.** Proton Chemical Shifts of Ruthenium(II) Octaethylporphyrin Complexes[a]

| Compd | Bridge protons | -*CH*$_2$CH$_3$ | -CH$_2$*CH*$_3$ | Pyridine α | Pyridine β | Pyridine γ |
|---|---|---|---|---|---|---|
| Ruthenium(II) carbonyl-octaethylporphyrin pyridinate | 9.75 s (4 H) | 3.88 q (16 H) | 1.82 t (24 H) | 1.07 m (2 H) | 4.76 m (2 H) | 5.65 m (1 H) |
| **2b** | 7.61 s (4 H) | 5.92 m (16 H) | 1.45 t (24 H) | 2.6 m (2 H) | 5.3 m (2 H) | nd |

[a] $CDCl_3$ solutions, chemical shifts in ppm downfield from tetramethylsilane; s = singlet, t = triplet, m = multiplet, q = quartet, nd = not detectable.

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(1) I. A. Cohen, *J. Amer. Chem. Soc.*, **91**, 1980 (1969); E. B. Fleischer and T. S. Srivastava, *ibid.*, **91**, 2403 (1969).

(2) M. Whalley, *J. Chem. Soc.*, 866 (1961); J. A. Elvidge, *ibid.*, 169 (1961).

(3) D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Amer. Chem. Soc.*, **93**, 2548 (1971).

(4) (a) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *ibid.*, **93**, 1820 (1971); M. Tsutsui, D. Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.*, **1**, 115 (1971); (b) B. C. Chow and I. A. Cohen, *Bioinorg. Chem.*, 1, 57 (1971).

(5) No other significant differences are apparent between the ir of **1** and **2a**.

(6) Loosely bound pyridine is lost from **2a** in the mass spectrometer. This is also observed for **1**.

(7) Lack of resolution of the methylene protons is probably caused by nonequivalence of the geminal protons due to axial dissymmetry. This has been observed for tin(II) octaethylporphyrin[8] as well as other similar compounds.[9]

(8) D. G. Whitten, J. C. Yau, and F. A. Carroll, *J. Amer. Chem. Soc.*, **93**, 2291 (1971).

(9) B. W. Roberts, A. Wissner, and R. R. Rimerman, *ibid.*, **91**, 6208 (1969); W. L. Meyer and R. B. Meyer, *ibid.*, **85**, 2170 (1963).

(10) This is indicated by the relatively sharp nmr spectrum of the dimer. The nmr also appears to rule out structures wherein the dimer results from nitrogen lone pair coordination to the ruthenium of a second molecule since such a structure would have multiple proton resonances unless rapid equilibration occurs.

(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley-Interscience, New York, N. Y., 1966, p 720.

(12) Interestingly Chow and Cohen[4b] report that irradiation of the carbonyl–tetraphenylporphyrin–ruthenium(II) complex in pyridine leads to carbon monoxide ejection and formation of the monomeric ruthenium(II) porphyrin dipyridinate. We have obtained a product having an identical spectrum with their product in preliminary experiments.

The quantum yield for the reaction is low ($1 \times 10^{-4}$ at λ 398 nm) and independent of concentration of **1** over the range $1\text{-}6 \times 10^{-5}$ *M*. We have found that **1** exhibits both delayed fluorescence and phosphorescence in degassed solutions at room temperature. The emission yield appears to be fairly concentration insensitive. These observations indicate that dimerization does not involve the luminescent states and suggests that a later-obtained species is the dimer precursor. The most likely path is outlined in eq 1-5,

$$\text{PyPRuCo} \xrightarrow{h\nu} \underbrace{\text{PyPRuCO}^{1*} \rightleftarrows \text{PyPRuCO}^{3*}}_{=\ \text{PyPRuCO}^{*}} \quad (1)$$

$$\text{PyPRuCO}^{*} \longrightarrow \text{PyPRuCO} + h\nu \quad (2)$$

$$\text{PyPRuCO}^{*} \longrightarrow \text{PyPRu} + \text{CO} \quad (3)$$

$$\text{PyPRu} + \text{PyPRuCO} \longrightarrow \text{PyPRu{=}RuPPy} + \text{CO} \quad (4)$$

$$\text{PyPRu} + \text{CO} \longrightarrow \text{PyPRuCO} \quad (5)$$

where Py = pyridine, P = porphyrin, and PyPRu=RuPPy is the dimer. Photoejection of CO followed by formation of the metal-metal bond, although novel for metalloporphyrin complexes, has been demonstrated for other metal complexes.[13,14]

The base complexed to the metalloporphyrin appears to exert a strong influence both in formation of the dimer and in determining its stability. As previously mentioned, **2a** forms readily upon irradiation of **1** in either benzene or pyridine. Irradiation of degassed benzene solutions of the imidazole, triethylamine, piperidine, or tetrahydrofuran complexes of ruthenium(II) carbonyloctaethylporphyrin leads to near-quantitative conversion to products having spectra similar to that of **2a**. The products from pyridine and the other nitrogen bases are stable indefinitely at room temperature.

However, in sealed tubes the tetrahydrofuran product reverts back to the starting material quantitatively within several hours. Irradiation of degassed benzene solutions of ruthenium(II) carbonyletioporphyrin I at 398 nm does not lead to **2** but rather to an unidentified product absorbing at 610 nm. This product is thermally stable at room temperature but readily reverts to starting material upon photolysis at 610 nm. The pyridine dimers **2a** and **2b** are stable indefinitely as solids in the dark; however, they are readily decomposed in solution by weak acids to yield products having characteristic metalloporphyrin spectra.

Further investigation is under way to elucidate full details of the mechanism of this reaction as well as to determine its scope and applicability to other metalloporphyrin systems.

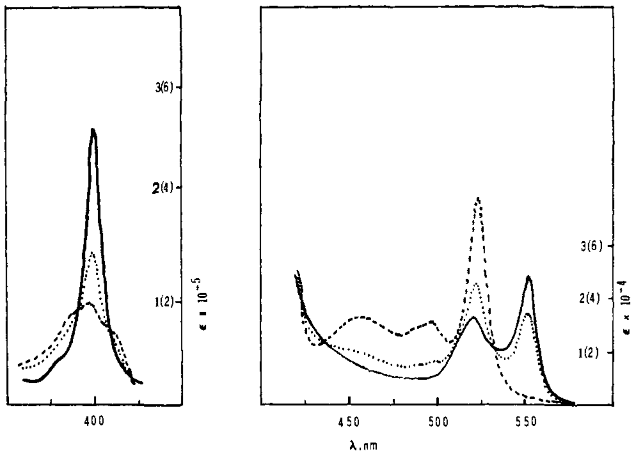

Figure 1. Photodimerization of ruthenium(II) carbonyletioporphyrin I pyridinate: (——) spectrum of **1** in pyridine; (···) intermediate conversion; (----) spectrum of photodimer **2a**. Numbers in parentheses refer to **2a**, others to **1**.

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The twisted phenyl rings in the latter complex probably preclude dimer formation on steric grounds.

(13) (a) E. Koerner von Gustorf and F. W. Grevels, *Fortsch. Chem. Forsch.*, **13**, 366 (1969); (b) W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, **3**, 730 (1964); (c) P. Chini, *Inorg. Chim. Acta*, **2**, 31 (1968); (d) K. L. Waters and W. M. Risen, *ibid.*, **3**, 129 (1969); (e) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 324.

(14) The source of the low reaction efficiency and possible details of the mechanism remain to be determined. It is possible that reaction 3 proceeds with very low efficiency or alternatively that cage recapture of CO is important. Possibly a CO-bridged species[13a] is intermediate in dimer formation.

(15) A. P. Sloan Foundation Fellow.

**G. Wayne Sovocool, Frederick R. Hopf, David G. Whitten***[15]
*Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514*

*Received February 28, 1972*

## Simultaneous Optical and Electron Spin Resonance Detection of the Primary Photoproduct P700 in Green Plant Photosynthesis[1]

*Sir:*

It has been known for some time that the initial steps in the photosynthetic mechanism of green plants, algae, and bacteria involve one-electron transfers.[2] These light-induced reactions create free-radical intermediates which may be detected by electron spin resonance (esr). Although these esr signals are thought to arise from components close to the primary photochemical reactions, the precise molecular identity of the free radicals has been a subject of much speculation and study.[3,4]

In certain photosynthetic bacteria (*e.g.*, *Rhodopseudomonas spheroides*), an exact correspondence of the light-induced esr signal with a bleaching at ~870 nm of a uniquely situated bacteriochlorophyll molecule has been demonstrated.[5-7] The situation is not nearly so convincing in green plant or algal systems. The early

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(2) E. Rabinowitch and Govindjee, "Photosynthesis," Wiley, New York, N. Y., 1969, pp 190–193.

(3) E. C. Weaver, *Annu. Rev. Plant Phys.*, **19**, 283 (1968).

(4) D. H. Kohl in "Biological Applications of Electron Spin Resonance," H. M. Swartz, J. R. Bolton, and D. C. Borg, Ed., Wiley, New York, N. Y., 1972.

(5) J. R. Bolton, R. K. Clayton, and D. W. Reed, *Photochem. Photobiol.*, **9**, 209 (1969).

(6) P. A. Loach and K. Walsh, *Biochemistry*, **8**, 1908 (1969).

(7) J. D. McElroy, G. Feher, and D. C. Mauzerall, *Biochim. Biophys. Acta*, **172**, 180 (1969).