Structure and Reactivity of Ruthenium(II) Porphyrin Complexes. Photochemical Ligand Ejection and Formation of Ruthenium Porphyrin Dimers

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Abstract. Ruthenium(II) carbonyloctaethylporphyrin pyridinate (**1**) in degassed pyridine solution is photochemically converted to ruthenium(II) octaethylporphyrin dipyridinate (**2**). The structure of **2** was determined by X-ray crystallography; the two pyridines are symmetrically coordinated to the ruthenium (Ru-N bond distance = 2.1 Å) which lies in the plane of the porphyrin. Irradiation of **1** in other solvents capable of complexing with the metal leads to the corresponding diligand complexes. However, irradiation of **1** in degassed benzene results only in incomplete and reversible decarbonylation. The air-stable crystalline solid **2**, when heated to 220° under vacuum, produces a microcrystalline dimeric solid which is soluble in benzene. The dimer is stable in benzene solution but is oxidized when in contact with air or dissolved in other solvents. Spectral data support the assignment of a dimer structure and suggest that the dimer has a strong metal-metal bond with the porphyrin rings eclipsed.

In recent years the study of metalloporphyrin complexes has been expanded by the synthesis of species containing second- and third-row transition metal ions,[2] including ruthenium(II, III).[3-6] The study of carbonyl complexes of ruthenium porphyrins is of general importance with respect to the carbonyl complexes of the corresponding hemes. Although the ruthenium and iron porphyrins exhibit marked chemical differences, both the ruthenium and iron complexes of the type M(CO)(base)(porphyrin) are presumably pseudooctahedral low-spin diamagnetic compounds.[7,8] Hence, studies of these systems, when M = Ru, are not totally unrelated to the biological hemes. Although many studies of iron(II) porphyrins have been conducted, they are made difficult by the extreme ease with which iron(II) is oxidized.

Such considerations led us to synthesize, as a more easily studied analog of the iron(II) porphyrins, carbonyl porphyrin derivatives of the similarly d^6 ruthenium(II). In a preliminary communication[6] we reported an investigation of the photochemistry of ruthenium(II) porphyrin carbonyl complexes. In this work we reported a facile photoreaction in which CO was ejected with subsequent formation of a porphyrin dimer. Contrary to previous indications, we find that the monomeric but diligated ruthenium(II) porphyrins are the first isolable products of CO photoejection in solution. In the present paper we report a more detailed investigation of this reaction with various ruthenium(II) porphyrins as well as a study of their thermal reactions. Stable ruthenium porphyrin dimers can be formed as subsequent products, but their formation results from a thermal reaction of the photoproduct. Along with the chemical study of these reactions, we report the complementary results of an X-ray study of octaethylporphyrinruthenium(II) dipyridinate, the initial product of CO photoejection from $Ru^{II}(CO)(py)OEP$ in pyridine.[9]

Experimental Section

Spectra. Ultraviolet and visible spectra were recorded either on a Cary Model 14 recording spectrophotometer or a Unicam Model SP-800B. Infrared spectra were recorded on a Perkin-Elmer Model 421. Proton nmr spectra were obtained through use of a Varian XL-100 with 10-mm sample tubes. All mass spectra were recorded on an AEI MS-902. Emission spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrophotometer. Electrochemical measurements were done with previously described equipment[10] in 0.1 *M* TBAH.

Materials. Octaethylporphyrin, etioporphyrin I, and tetraphenylporphine were prepared as described by literature methods. Ruthenium(II) carbonyl porphyrins were prepared by the method of Tsutsui, *et al.*[4] Pyridine (reagent grade) was distilled from potassium hydroxide and calcium oxide prior to use. Other solvents (except spectrograde solvents) were purified by distillation.

Preparative Photodecarbonylation Reactions. Irradiations were carried out on solutions (~0.01 *M*) of ruthenium(II) carbonyl porphyrins in an appropriate ligating solvent. Pyrex ampoules of solution were degassed by at least three freeze-pump-thaw cycles and irradiated by a medium-pressure mercury lamp (450-W Hanovia) with a Pyrex filter until reaction was complete. The diligate product, which precipitated as reaction occurred, was filtered on a glass frit and washed with cold solvent, then vacuum dried at room temperature for 24 hr.

Formation of the Solid State Thermal Product. A small quantity of ruthenium(II) porphyrin dipyridinate was introduced into a heavy-walled ampoule attached to a standard taper grease trap for attachment to a high vacuum line. The sample was opened to the vacuum and heated in an oil bath to 220°. This temperature was maintained for several hours, depending on the size of the sample. The sample was then sealed on the vacuum line. Sealed ampoules of thermal product were opened and immediately dissolved in the appropriate solvent.

Preparation of $Ru^{II}(py)_2OEP$. A suspension of 0.05 g of $Ru^{II}(CO)OEP$ in 6 ml of pyridine was degassed by three freeze-pump-thaw cycles, then sealed and strapped to a medium-pressure mercury lamp (Pyrex filter) and irradiated for 40 hr. The crystals of quite insoluble $Ru^{II}(py)_2OEP$ which separated as reaction progressed were filtered and washed with cold pyridine and vacuum dried for 24 hr. The ir spectrum (KBr disk) of the dipyridinate shows the usual porphyrin bands but has completely lost the intense ruthenium-carbonyl stretching band at 1934 cm^{-1}.

Anal. Calcd for $C_{46}H_{54}N_6Ru$: C, 69.76; H, 6.87; N, 10.61; Ru, 12.76. Found: C, 71.30; H, 7.30; N, 9.17; Ru, 10.83.

Similar results were obtained for the synthesis of $Ru^{II}(py)_2$etio I.

Anal. Calcd for $C_{42}H_{46}N_6Ru$: C, 68.55; H, 6.30; N, 11.42; Ru, 13.73. Found: C, 68.02; H, 6.08; N, 12.22; Ru, 14.90.

Preparation of $Ru^{II}(DMSO)_2OEP$. A suspension of 0.05 g of $Ru^{II}(CO)OEP$ in 6 ml of purified DMSO was degassed by four freeze-pump-thaw cycles, then sealed and irradiated for 50 hr with a medium-pressure mercury lamp (Pyrex filter). The crystals of solid $Ru^{II}(DMSO)_2OEP$ were isolated (slow reversion to carbonyl compound will occur) immediately after irradiation, washed with solvent, and vacuum dried at 50° for 48 hr.

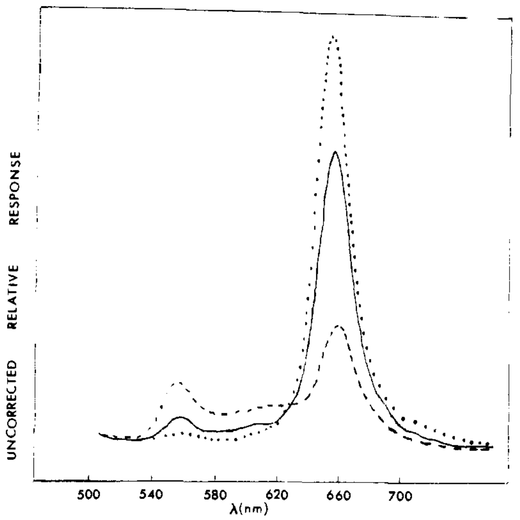


Figure 1. Uncorrected emission spectra of $Ru^{II}(CO)(py)OEP$ in pyridine: (····) −10°, (—) 25°, (- - - -) 90°.

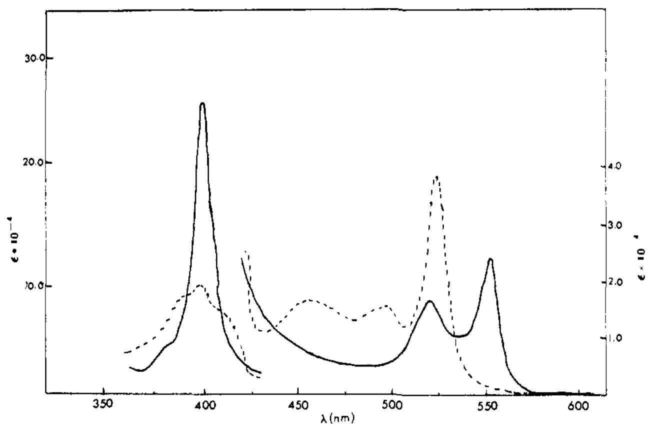


Figure 2. Photodecarbonylation of ruthenium(II) carbonyloctaethylporphyrin pyridinate: (—) spectrum of **1** in pyridine; (- - - -) spectrum of **2** in pyridine.

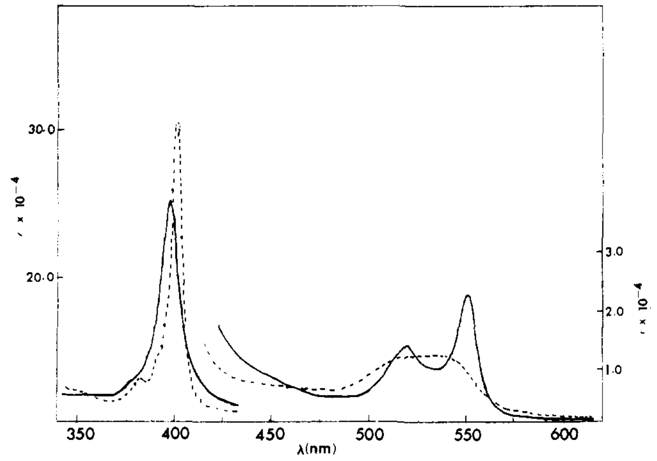


Figure 3. Photodecarbonylation of ruthenium(II) carbonyloctaethylporphyrin: (—) spectrum of **1** in DMSO; (- - - -) spectrum of **3** in DMSO.

Anal. Calcd for $C_{40}H_{56}N_4S_2O_2Ru$: C, 60.81; H, 7.14; N, 7.09; S, 8.11; Ru, 12.79. Found: C, 59.27; H, 6.82; N, 7.13; S, 7.56; Ru, 12.22.

Results and Discussion

Photochemistry of Octaethylporphyrinruthenium(II) Carbonyl Complexes. Undegassed solutions of octaethylporphyrinruthenium(II) carbonyl complexes (**1**) are relatively stable to light. Upon prolonged irradiation slow decomposition to as yet unidentified products is observed. No luminescence can be detected from undegassed solutions of **1** in most solvents, a notable exception being dimethyl sulfoxide solutions where relatively strong emission is observed unless oxygen or air is passed through the solution during irradiation. Degassed solutions of **1** exhibit relatively prominent luminescence which is strongly temperature dependent (Figure 1). The emission evidently consists of fluorescence (λ_{max} 556 nm) and phosphorescence (λ_{max} 658 nm). Since the fluorescence appears to vanish completely as the temperature is lowered below *ca.* −10°, the emission is due to prompt phosphorescence and thermally activated ("E-type") delayed fluorescence. The observation of similar phosphorescence from room temperature solutions has been previously reported for platinum and palladium complexes of the porphyrins,[11] as well as with other ruthenium(II) complexes such as the tris(2,2′-bipyridine)ruthenium(II) cation.[12] Here apparently as in the other cases the heavy metal produces relaxation of the spin forbiddenness of the $T^* \rightarrow S^0$ transition.

Irradiation of degassed solutions of **1** in pyridine, dimethyl sulfoxide, tetrahydrofuran, and aromatic and aliphatic amines results in formation of photoproducts having electronic spectra decidedly different from the starting material. Figures 2 and 3 show the conversion of **1** to photoproduct in pyridine and dimethyl sulfoxide, respectively. In both of these solvents product formation is complete and the photoproduct can be isolated. In more weakly ligating solvents such as tetrahydrofuran, photoproduct formation is thermally reversible and it is not possible to isolate the product at room temperature.

Irradiation of the freshly prepared and dried monopyridinate of **1**, $Ru^{II}(CO)(py)OEP$, in degassed solution of dry benzene leads only to partial (<5%) formation of **2**. However, in the presence of trace amounts of moisture (introduced in either sample or solvent) photolysis of the monopyridinate leads to formation of a product having a spectrum indistinguishable from that produced in pyridine. The reaction proceeds with a low quantum efficiency (~1×10^{-4} at λ 398 nm) in benzene-pyridine (1%) and in pyridine; the quantum efficiency is insensitive to concentration of the starting material and to pyridine concentrations in the range of 1% or higher.

Characterization of Photoproducts from 1. The photoproduct from **1** in pyridine (**2**) has been characterized by spectral means and by an X-ray crystal structure to be the dipyridinate complex of octaethylporphyrinruthenium(II). The ir spectra of the photoproducts from pyridine (**2**) and DMSO (**3**) both show typical porphyrin frequencies together with loss of the characteristic metal bound CO stretching frequency. Therefore in both cases CO has been lost as a consequence of photolysis. Table I compares nmr spectra of photoproduct **2** with the starting complex. The values listed in Table I were obtained with freshly prepared deuteriobenzene solutions and differ substantially from those previously reported for deuteriochloroform solutions. Evidently in chloroform solutions of **2**, ready oxidation generates small amounts (spectrally undetectable) of the ruthenium(III) complex which induces paramagnetic shifts and broadening of the nmr spectrum of **2**. In the unbroadened spectrum obtained for deuteriobenzene solutions of **2**, it is clear that the complex shows only the protons of the parent OEP skeleton and bound pyridine and that the porphyrin:bound pyridine ratio is 1:2. In contrast to the nmr spectrum of **2** which is completely consistent with the structure of a monomeric ruthenium(II) porphyrin dipyridinate, the mass spectrum of **2** shows as its most prominent peaks those of mass 1268 and

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

Compound	Bridge protons	-$CH_2$$CH_3$	-$CH_2$$CH_3$	Pyridine α	Pyridine β	Pyridine γ
Ruthenium(II) carbonyl octaethylporphyrin pyridinate	10.18 s (4 H)	3.97 q (16 H)	1.92 t (24 H)	1.26 d (2 H)	4.05 t (2 H)	4.56 t (1 H)
Ruthenium(II) octaethylporphyrin dipyridinate	9.65 s (4 H)	3.88 q (16 H)	1.92 t (24 H)	2.16 d (4 H)	4.08 t (4 H)	4.63 t (2 H)

[a] Benzene-d_6 solutions, chemical shifts in ppm downfield from tetramethylsilane as internal standard: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

634 corresponding to the dimer of ruthenium(II) porphyrin without ligands and the monomer, also without bound pyridine. The region around 634 contains both the isotope pattern for monomeric ruthenium porphyrin and doubly charged dimeric fragments. In addition there are also peaks near 422 with an isotope pattern corresponding to triply charged dimer fragments. In contrast the mass spectrum of starting carbonyl complex **1** shows only groups of monomer ion corresponding both to $Ru^{II}OEP$ (634, relative intensity 1.0) and $Ru^{II}(CO)OEP$ (662, relative intensity 0.2). The mass spectrum of the DMSO photoproduct **3** shows predominantly monomeric ion groupings for $Ru^{II}OEP$ without ligands (634), although a trace of dimeric ions can be detected. That the photoproduct **2**, obtained in pyridine, is $Ru^{II}(py)_2OEP$ and not a dimer has been clearly shown by X-ray structure determination.[13]

The six-coordinate $Ru^{II}(py)_2OEP$ molecule is displayed in Figure 4. Also displayed in Figure 4 are the identifying labels assigned to the atoms and the crystallographically independent bond distances in the porphinato core, the coordination group, and the axial ligands. Key features of the structure include the near flatness of the porphinato core and the perpendicular coordination of two pyridines which are essentially equivalent with Ru-N_{py} bonds of *ca.* 2.1 Å. The molecules are well separated in the crystal with the closest Ru-Ru contacts being those required by a unit cell translation (9.69 Å). Other Ru-Ru distances range from 10.07 Å. Intermolecular contacts range upward from the 3.54 Å contacts observed between two partially overlapping pyridine rings. Details of the structure, together with a listing of the structure factor amplitudes will follow these pages in the microfilm edition.

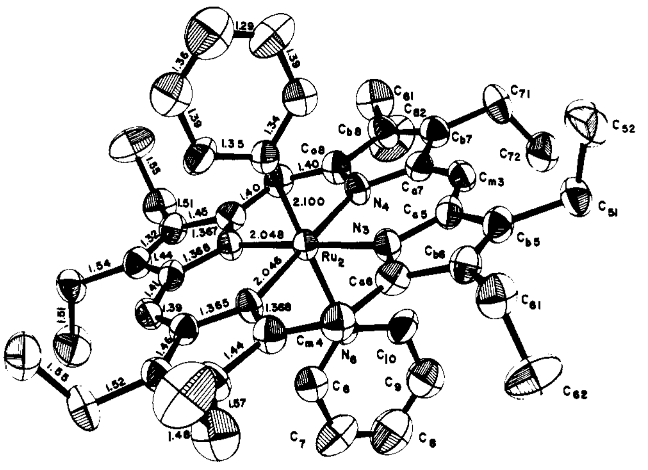


Figure 4. Computer-drawn model in perspective of one of the two independent centrosymmetric molecules as it exists in the crystal. Also shown is the numbering system employed for the atoms and the crystallographically independent bond distances.

The electronic spectrum of **2** (Figure 2) contrasts sharply with those of other octahedral divalent metal complexes of porphyrins as well as with the spectra of ruthenium(II) complexes of **1** and **3**. A probable reason for this "altered" metalloporphyrin spectrum of **2** is the presence of low lying d → π* (metal-ligand charge transfer) states in this ruthenium(II) complex. It has been well established that prominent d → π* transitions occur in the region 400-500 nm in other ruthenium(II) complexes with nitrogen ligands, most notably in the tris(2,2′-bipyridine)ruthenium(II) cation and related complexes. These transitions are of comparable intensity to the usual metalloporphyrin π → π* transitions but are generally much broader. The complex spectrum for **2** is probably a result of several transitions to "mixed" levels formed from both π,π* and d,π* states. That such transitions are lacking in **1** and **3** can be accounted for by the presence of the back-bonding ligands CO and DMSO in these complexes. Presumably, the back-bonding ligand lowers the energy of the ruthenium d electrons and raises the energy of the d → π* transitions out of the visible-near-uv region. The concurrent change in site and ease of oxidation induced by addition of back-bonding ligands to ruthenium(II) porphyrins is consistent with this explanation.[14]

Reactivity of Ru^{II}(ligand)$_2$OEP Complexes. Diligand complexes **2** and **3** both undergo ligand substitution with CO upon bubbling CO through solutions in benzene (rapid), pyridine (slow), and DMSO (slow). Heating of **2** in DMSO results in slow formation of **3**. In other solvents such as chloroform, methylene chloride, and *N*-methylformamide heating of nondegassed solutions of **2** results in rapid oxidation to the ruthenium(III) complex.

Our initial conclusion that the photoproduct from 1 was a dimer was based primarily on evidence from nmr and mass spectra. The nmr spectrum originally reported[6] (*vide supra*) was probably distorted by the paramagnetic effect of a small amount (spectrally undetectable) of oxidized ruthenium(III) porphyrin in chloroform. The persistence of dimeric mass spectra, however, suggested that dimers might well be formed by thermolysis of initial photoproduct **2** during introduction into the direct inlet of the mass spectrometer. Therefore, we investigated thermolysis of **2**, **3**, and the dipyridinate of ruthenium(II) tetraphenylporphine under high vacuum.

Heating of **2** or **3** in degassed evacuated tubes in the solid state at 220° results in readily observable changes both in the crystal structure and in color (from brown to green). The solids produced from **2** and **3** are identical. Treatment of the solid (**4**) with carbon monoxide results in rapid uptake of CO to yield starting compound **1**. Treatment of **4** with pyridine or DMSO regenerates **2** and **3**, respectively. Thermal product **4** dissolves in benzene to give a purple solution (Figure 5) which is stable indefinitely in a stoppered cuvette. X-Ray powder patterns were determined for **2** and for samples of **4** prepared by thermolysis of finely ground **2**.

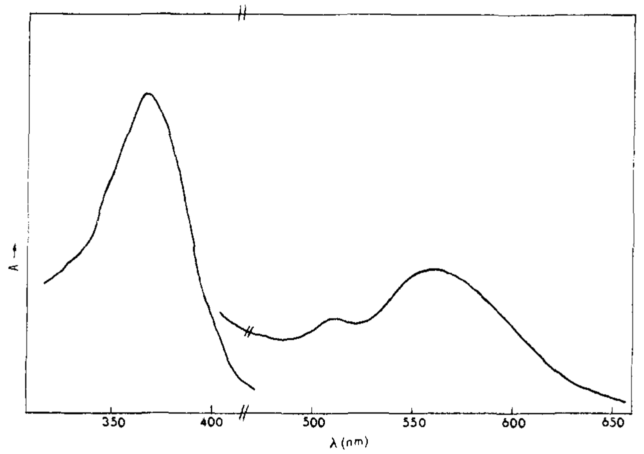


Figure 5. Ultraviolet-visible spectrum of the solid state thermal product of $Ru^{II}(py)_2OEP$ in benzene.

Both samples exhibited crystalline powder patterns; however, the patterns for **2** and **4** were distinctly different. In comparison, heating of the dipyridinate of ruthenium(II) tetraphenylporphine under the same conditions results in little discernible chemical change. The spectrum of the "product" from this reaction dissolved in benzene is not appreciably altered from the starting material.

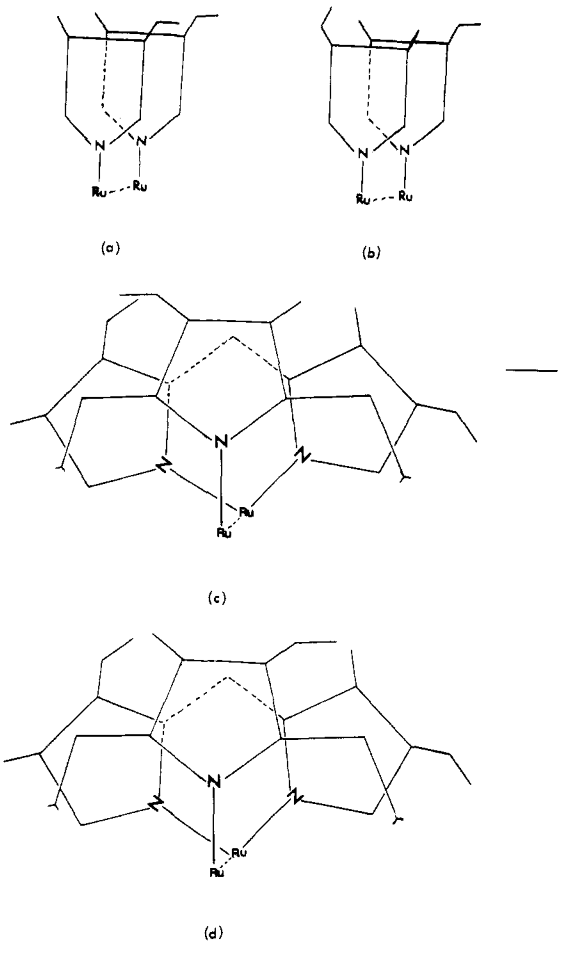


Figure 6. Possible solid state thermal dimer structures of (RuEtio I)$_2$: (a) methyl-methyl eclipsed, (b) methyl-ethyl eclipsed, (c) methyl-methyl staggered, (d) methyl-ethyl staggered.

The solid thermal product shows predominantly dimer peaks in the mass spectrum and investigation of the nmr spectrum of deuteriobenzene solutions of **4** indicates that the product is a dimer. Table II gives nmr data for deuteriobenzene solutions of the solids produced by thermal reactions of **2** and the corresponding etioporphyrin I complex. Scheme I summarizes the interconversion of the different Ru(II) porphyrin complexes. The octaethylporphyrin complex **4** shows only the three types of protons expected for the parent metalloporphyrin: a singlet for the bridge protons, a methyl triplet, and the methylene resonances of the ethyl group. The methylene protons are diastereotopic; decoupling of these protons gives the expected AB pattern. These data are thus consistent either with a dimer or with a complex in which the metal is out of plane to one side as has been observed for tin(IV) and lead(II) porphyrins. The etioporphyrin I complex (**5**) shows a somewhat more complex spectrum which can be accounted for completely by protons of the parent porphyrin. Here again there is a singlet for the bridge protons. However, the protons for the methylene and methyl protons of the ethyl groups show somewhat more complex patterns. There are two overlapping methyl signals as can be shown by decoupling. The methylene protons are once again diastereotopic and even on decoupling the AB pattern obtained shows the broadening expected for two overlapping signals. However, the key resonances appear to be the two sharp singlets for the ring-methyl groups which are of about equal intensity. The nmr spectrum indicates that the product has a dimeric structure and moreover that there are two dimers for **5** obtained in approximately equal amounts. The most consistent explanation of the spectrum is that the dimers have either staggered or eclipsed structures such as shown in Figure 6. The nmr spectrum indicates that for **5** there must be two structures—the set, methyl-methyl eclipsed (**5a**) and methyl-ethyl eclipsed (**5b**), or the corresponding "staggered" set. Each of these structures should have a single but different set of "etioporphyrin" protons. The ring-methyl and ethylmethylene should be different while the ethyl-methyl would be less shifted between the two isomers and the bridge protons

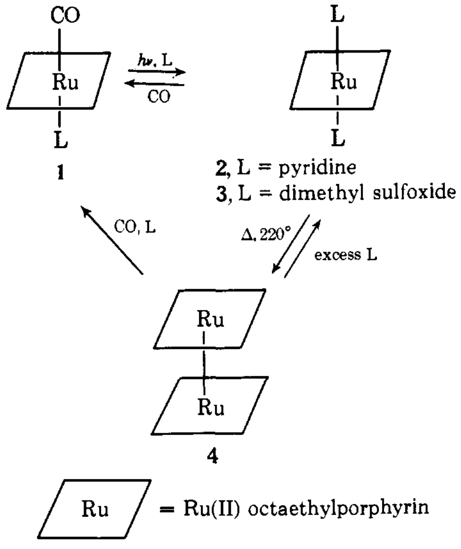
Table II. Proton Chemical Shifts of Solid State Thermal Products of $Ru^{II}(py)_2OEP$ and $Ru^{II}(py)_2Etio$ I[a]

Compound	Bridge protons	Ring—CH_3	-$\mathit{CH_2}CH_3$	-$CH_2\mathit{CH_3}$
Thermal product of $Ru^{II}(py)_2OEP$	9.40 s (8 H)		4.35 m (16 H)[b] 4.01 m (16 H)	1.86 t (48 H)
Thermal product of $Ru^{II}(py)_2$ Etio I	9.27 s (8 H)	3.54 s (12 H)[c] 3.49 s (12 H)	4.35 m (8 H)[d] 4.02 m (8 H)	1.86 q (24 H)[e]

[a] Benzene-d_6 solutions, chemical shifts in ppm downfield from tetramethylsilane as internal standard; s = singlet, t = triplet, q = quartet, m = multiplet. [b] To illustrate the diastereotopic nature of the methylene protons, decoupling was done at the frequency of the terminal methyl resonances. This caused the complex multiplet pattern for the methylene protons to collapse to a simple AB pattern. [c] Decoupling at either the resonance frequency of the methylene or terminal ethyl-methyl protons caused no change in these signals. [d] Decoupling at the resonance frequency of the ethyl-methyl protons caused these complex multiplets to change to a slightly broadened AB type pattern. This is evidently due to two nearly identical overlapping AB patterns. [e] Although the ethyl-methyl protons of the ethyl groups appear as a slightly distorted quartet, the signal is due to two distinct "types" of terminal ethyl-methyl protons as indicated by resonance decoupling. During decoupling at the center of the methylene resonance frequency, the quartet changes to two sharp singlets of nearly equal intensity at δ 1.90 and 1.81.

should have nearly the same chemical shifts. Since the bridge protons of the dimer are shifted only slightly upfield compared to those in the monomeric metalloporphyrin precursors, it appears that the eclipsed structure is the correct structure for the dimer since ring current effects in the "staggered" structure would be expected to produce strong shielding and hence upfield shifts of a magnitude which are not observed. The observed shifts are very close to those observed between benzene and [2.2]paracyclophane and [3.3]paracyclophane; in the latter compounds eclipsed structures are indicated for the benzene rings.[15,16]

Scheme I. Interconversion of Ruthenium(II) Porphyrins



Considerations of orbital models for metal-metal bonding also indicate an eclipsed structure should be preferred for the dimer. Using the model developed by Cotton[17] for the octahalodirhenate dianion the ground state configuration of ruthenium d electrons would be $\sigma^2\pi^4\delta^2\sigma_n^4$, where σ_n represents the nonbonding levels. Therefore in an eclipsed structure there should be a net of four bonds, three of which would not be present in the "staggered" dimer. This model also predicts that the metal-metal bonding should result in a short Ru-Ru distance with very strong bonding.[18] That much stronger bonding occurs in this dimer than in previously prepared porphyrin dimers[20-22] is indicated by several considerations.

First, with etioporphyrin I dimers **5** there are two isomers formed in approximately equal quantities even though the totally eclipsed structure **5a** is probably less stable than structure **5b**. This suggests that formation of the dimers is kinetically controlled. The fact that no changes in product distribution occur in the benzene solution nmr spectrum indicates that equilibration does not occur at room temperature and indicates fairly strong bonding. Since no change in the spectrum occurs over several hours, a minimum ΔG^* at room temperature is 25 kcal/mol. Moreover the fact that dimer peaks are still the most prominent when the sample is introduced into the mass spectrometer at 280° allows a minimum estimate of ΔG^* (from absolute rate theory, and assuming a rate constant k_{dec} of 1 sec^{-1}) of 33 kcal/mol. Since the entropy associated with dimer formation in other porphyrins is usually *ca.* −20 eu,[20,21] an estimate that $\Delta H^* = 44$ kcal/mol as a minimum activation enthalpy for dimer decomposition indicates that metal-metal bonding is very strong. This minimum value for the dimer enthalpy is much larger than that associated with formation of dimers from free base porphyrins and other metalloporphyrins where metal-metal bonding is not indicated.

We are continuing to investigate the properties and reactions of the ruthenium porphyrin dimer as well as to probe the possibility of similar dimer formation with other metal complexes. Preliminary indications from cyclic voltammetry studies of the dimer are that several reversible oxidations occur in a narrow range (between 0 and 1.2 volts *vs.* ssce) as might be anticipated for an electronic configuration similar to that proposed above.

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Supplementary Material Available. Details of the structure of $Ru^{II}(py)_2OEP$ and its determination together with a listing of structure factor amplitudes (×10) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for $6.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-277.

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(9) Abbreviations used: H_2OEP = octaethylporphyrin, OEP = octaethylporphyrin dianion, H_2Etio I = etioporphyrin I, Etio I = etioporphyrin I dianion, H_2TPP = tetraphenylporphine, TPP = tetraphenylporphine dianion, py = pyridine, EtOH = ethanol, L = donator ligand, DMSO = dimethyl sulfoxide, TBAH = tetrabutylammonium hexafluorophosphate.
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