Photochemistry of Biologically Important Transition Metal Complexes. II. Carbonylpiperidinetetraphenylporphine Complexes of Iron(II) and Ruthenium(II)

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Absorptionsspektren, sichtbar und ultraviolett / Emissionsspektren / Komplexverbindungen / Photochemie

Carbonylpiperidinetetraphenylporphineiron(II) and dipiperidinetetraphenylporphineiron(II) do not emit the characteristic porphyrin phosphorescence. It is suggested that the porphyrin singlets initially excited undergo an efficient radiationless transition to an excited state which lies below the lowest porphyrin triplet. It is concluded that this lower excited state initiates the release of coordinated CO which has been observed for a variety of biologically important carbonylporphyrins of iron(II). It is assumed that the reactive state is either an excited CT or, more likely, a LF state. If iron(II) is replaced by the homologous ruthenium(II) the lowest LF excited state lies apparently at higher energies than the lowest porphyrin triplet due to the larger LF splitting of the heavier ruthenium. Hence carbonylpiperidinetetraphenylporphineruthenium(II) dissolved in piperidine shows the typical porphyrin phosphorescence, but undergoes also a simultaneous photosubstitution of CO by piperidine with low efficiency. Quantum yields of CO release and relative emission intensities were determined at two irradiating wavelengths (412 and 530 nm) and at two temperatures (25 °C and 80 °C). The results led to the suggestion that the reactive LF state can be populated from the lower porphyrin triplet by thermal activation. In addition to this thermally activated photolysis a temperature independent contribution seems to be important at higher excitation energies. It is assumed that the deactivation cascade starting from higher excited singlets of the porphyrin ligand includes the population of the reactive LF state before the lowest porphyrin triplet is reached. It is also possible that it is not a LF state but a low-lying CT state which is responsible for the photoreactivity.

Carbonylpiperidintetraphenylporphineisen(II) und Dipiperidintetraphenylporphineisen(II) zeigen nicht die charakteristische Porphyrin-phosphoreszenz. Es wird angenommen, daß die Porphyrinsinguletts, die zunächst angeregt werden, einer raschen strahlungslosen Desaktivierung zu einem angeregten LF-Zustand unterliegen, der unter dem niedrigsten Porphyrintriplett liegt. Dieser LF-Zustand ist auch der reaktive Zustand, der die Abspaltung der koordinierten CO-Liganden auslöst, wie sie für viele biologisch wichtigen Carbonylporphyrin-komplexe von Eisen(II) beobachtet worden ist. Es ist allerdings auch möglich, daß der reaktive Zustand nicht ein LF- sondern ein CT-Zustand ist. Wenn Eisen(II) durch Ruthenium(II) ersetzt wird, dann liegt der niedrigste LF-Zustand, bedingt durch die größere LF-Aufspaltung durch das schwerere Ruthenium, offensichtlich bei höheren Energien als das niedrigste Porphyrintriplett. Daher zeigt Carbonyl-piperidintetraphenylporphinruthenium(II), gelöst in Piperidin, die typische Porphyrinphosphoreszenz, aber unterliegt außerdem auch einer Photosubstitution von CO durch Piperidin. Quantenausbeuten der CO-Substitution und relative Emissionsintensitäten wurden bei zwei Anregungswellenlängen (412 und 530 nm) und bei zwei Temperaturen bestimmt (25 °C und 80 °C). Die Ergebnisse führten zu der Annahme, daß der reaktive LF-Zustand vom niedrigsten Porphyrintriplett durch thermische Aktivierung besetzt werden kann. Neben diesem thermisch aktivierten Prozeß führt insbesondere bei höheren Anregungsenergien auch ein temperaturunabhängiger Vorgang zur Photolyse. Es wird angenommen, daß die Desaktivierungskaskade, die von höher angeregten Singuletts des Porphyrinliganden ausgeht, die Besetzung des reaktiven LF-Zustandes einschließt, ehe das niedrigste Porphyrintriplett erreicht wird. Allerdings kann nicht ausgeschlossen werden, daß der reaktive angeregte Zustand ein niedrig liegender CT-Zustand ist.

Introduction

Upon exposure to light hemoglobin carbon monoxide, myoglobin carbon monoxide and related carbonyl porphyrin complexes of hexacoordinated low-spin Fe(II) release the coordinated CO ligand. In 1896 this reaction was discovered [1] and has been investigated extensively until now [2]. Warburg et al. determined quantum yields of this reaction already in the 1920s [3, 4]. Nevertheless it is unknown which excited state does initiate this photodissociation.

The difficulty to identify the photoactive excited states of these porphyrin complexes is associated with the fact that their electronic spectra are dominated by the very intense absorption bands of the porphyrin ligand [5]. Any other absorptions as CT bands and particularly LF bands which should be of low intensity have not been identified. The photosubstitution occurs by light absorption of the porphyrin ligand. Since the quantum yields are very high and independent of the exciting wavelength [6, 7] one may assume that the lowest porphyrin triplet is the lowest excited state of the

complex and leads to the photoreaction. However, it is difficult to explain how this excited state may initiate the observed substitution of CO.

In a theoretical study it has been suggested that a low-lying LF excited state of the central iron is responsible for the light sensitivity [5]. The analogy of the photoreactions of cyanide [8] and carbon monoxide [2] porphyrin complexes of Fe(II) to those of $Fe(CN)_6^{4-}$ and $Fe(CN)_5CO^{3-}$ [9] support this assumption since excited LF states of the latter ones have been shown to lead to a substitution of CN^- and CO. However, conclusive evidence has not yet been obtained.

It has been shown, particularly by Crosby [10], that the relative ordering of excited states of different origin as intraligand, CT, and LF states can be changed by the appropriate choice of ligands and metals. Since this ordering has an important influence on the photochemical and photophysical behavior of metal complexes, under suitable conditions such variations can be used to identify the reactive excited states. This approach has recently led to the identification of the

reactive excited state of cyanocobalamin [11]. We expected that the same approach can be used to detect the reactive state of carbonylporphyrin complexes of Fe(II). Our expectation was based on an important observation which has been recently made by Whitten et al. [12, 13]. They have shown that the complex carbonyloctaethylporphyrinpyridineruthenium(II) is luminescent and undergoes a simultaneous photosubstitution of CO. The relationship between reactive and emitting state was not known. The present investigation of the photophysical and photochemical behavior of carbonylporphyrin complexes of iron(II) and ruthenium(II) was undertaken to identify the nature of the excited state which initiates the photochemical substitution of CO.

Experimental Section

Materials. (Piperidine)$_2$(TPP)Fe(II)*) was prepared according to a published procedure [14, 15].

(CO)(piperidine)(TPP)Fe(II) · 0.4 CH$_2$Cl$_2$. At 0 °C (piperidine)$_2$ · (TPP)Fe(II) was dissolved in CH$_2$Cl$_2$ saturated with CO. A vigorous CO stream was bubbled through the solution until the solvent was removed by the CO stream. A wet solid was obtained, which was washed with pentane saturated with CO, and dried in a stream of CO. The IR spectrum (KBr disk) shows the usual porphyrin bands and the characteristic CO stretching band at 1978 cm^{-1}. Anal. Calcd. for (CO)(piperidine)(TPP)Fe(II) · 0.4 CH$_2$Cl$_2$: C, 74.21; N, 8.58; H, 4.92. Found: C, 74.21; N, 8.57; H, 5.27. (CO)(piperidine) · (TPP)Ru(II) was prepared by the method of Tsutsui et al. [16, 17]. The IR spectrum (KBr disk) shows the porphyrin bands and the CO stretching band at 1948 cm^{-1}. Anal. Calcd. for (CO)(piperidine) · (TPP)Ru(II): C, 72.62; N, 8.46; H, 4.75. Found: C, 72.48; N, 8.50; H, 4.92.

Photolysis procedure. The light source used was a 450 W Osram high-pressure xenon lamp XBO 450. A Schott WG 395 filter was used for irradiation with light of wavelengths longer than 370 nm. A Schott interference filter PIL 406 was used for the irradiation around 406 nm. The filter combination Schott OG 515 and Balzers K3 transmitted light between 510 and 550 nm with a maximum at 530 nm. The photolyses were carried out in spectrophotometer cells. For quantum-yield measurements the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Quantum yields were determined with a precision of ±10%. Absorbed light intensities were determined by Ferrioxalate [18] and Reineckate [19] actinometry.

Measurements. Visible and ultraviolet spectra were measured with a Cary 14 recording spectrophotometer and a Zeiss PMQ II spectrophotometer for measurements at selected wavelengths. Infrared spectra were measured with a Perkin Elmer 325 IR spectrophotometer. Samples were KBr pellets.

Emission spectra were recorded on an Aminco spectrophotofluorometer and a modified apparatus described elsewhere [20]. This apparatus was equipped with a cooled RCA C7164 R photomultiplier for the detection of low emission intensities in the red. Compounds were in the solid state or dissolved in piperidine. (CO)(piperidine)(TPP)Fe(II) was in the solid state or dissolved in CH$_2$Cl$_2$ saturated with CO. The temperature dependence of relative emission yield was determined using solutions of the same absorbance at constant slit widths. The precision of these measurements was ±5%.

The photochemical and emission experiments were carried out without exclusion of oxygen. It was shown that removing oxygen from the solutions affected the measurements, but the reproducibility was not very good.

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*) The abbrevation TPP designates meso-tetraphenylporphine.

Results

The preparation of (CO)(piperidine)(TPP)Fe(II) has not yet been reported, but according to published observations [21, 22] its synthesis should be possible. It was achieved by the reaction of (piperidine)$_2$(TPP)Fe(II) [14, 15] with CO in CH$_2$Cl$_2$. However, the resulting carbonyl complex is not very stable. In noncoordinating solvents as CH$_2$Cl$_2$ or benzene it seems only to be stable if an excess of CO is present. In coordinating solvents as piperidine the CO ligand may be replaced by a solvent molecule [21, 22]. The absorption spectrum of (CO)(piperidine)(TPP)Fe(II) dissolved in CH$_2$Cl$_2$ which was saturated with carbon monoxide is similar to that of (piperidine)$_2$(TPP)Fe(II) [23]. The maxima of the γ-bands of both complexes appear at 422 nm and 425 nm respectively. In solution or in the solid state neither the carbonyl nor the dipiperidine complex did show any detectable emission at temperatures down to 77 K and at different exciting wavelengths including the γ-band and the region of the α and β bands.

The complex (CO)(piperidine)(TPP)Ru(II) was prepared in analogy to other carbonylporphyrin complexes of Ru(II) [16, 17]. Its absorption spectrum (Fig. 1) shows the α ($\lambda_{max} = 567$ nm, $\varepsilon = 3.3 \cdot 10^3$), β ($\lambda_{max} = 531$ nm, $\varepsilon = 1.7 \cdot 10^4$) and γ or Soret ($\lambda_{max} = 412$ nm, $\varepsilon = 2.7 \cdot 10^5$) bands of the porphyrin ligand. In analogy to other carbonyltetraphenylporphine complexes of Ru(II) [16, 17] only the β and γ bands show well developed maxima. In solutions of piperidine the complex (CO)(piperidine)(TPP)Ru(II) was thermally stable. However, upon irradiation with light of wavelengths longer than 370 nm CO was released as indicated by the IR spectrum of the photolysis product which did not exhibit the typical absorption of the CO stretching vibration.
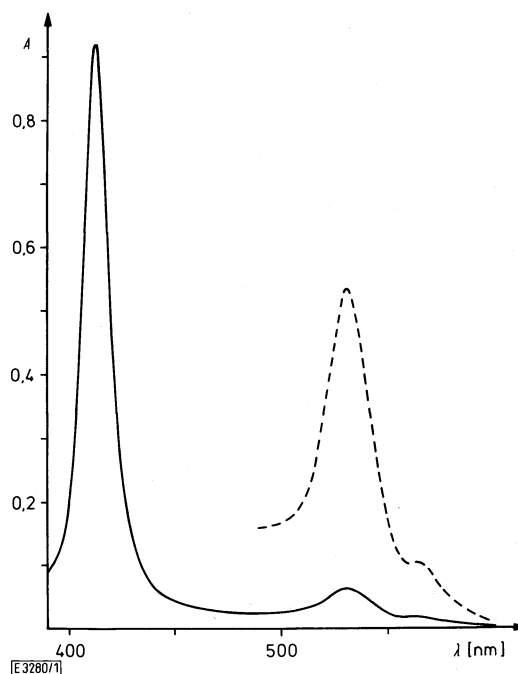

Fig. 1
——— Absorption spectrum of 3.35 · 10^{-6} M
(CO)(piperidine)(TPP)Ru(II) in piperidine;
– – – – Absorption spectrum of 3.14 · 10^{-5} M
(CO)(piperidine)(TPP)Ru(II) in piperidine

The CO ligand was apparently replaced by piperidine under formation of (piperidine)$_2$(TPP)Ru(II). The pattern of the spectral variations which accompanied the photoreaction (Fig. 2) was similar to that which has been observed during the photolysis of (CO)(pyridine)(octaethylporphyrin)Ru(II) in pyridine which proceeds under substitution of CO by pyridine [12, 13]. After prolonged

irradiation of (CO)(piperidine)(TPP)Ru(II) the spectrum did not change anymore. It is assumed that the formation of (piperidine)$_2$ · (TPP)Ru(II) was complete. If light absorption of the carbonyl complex was complete the photolysis followed a zeroth order kinetics up to about 20% of photolyzed starting complex. The amount of conversion was determined by the change of extinction at 412 nm. Quantum yields were determined at 406 nm and 530 nm irradiating wavelengths and at 25 °C and 80 °C (Table 1).

Table 1

Quantum yields of CO release and relative emission intensities for (CO)(piperidine)(TPP)Ru(II) in piperidine

Excitation λ (nm)	T [°C]	Quantum yield	Relative emission intensity
530	25	$2.5 \cdot 10^{-6}$	100
	80	$1.5 \cdot 10^{-4}$	66
410	25	$5.9 \cdot 10^{-5}$	100
	80	$1.6 \cdot 10^{-4}$	66

In a solution of piperidine or in the solid state (CO)(piperidine) · (TPP)Ru(II) showed the typical porphyrin phosphorescence (Fig. 3). The 0-0 band appeared at 652 nm. The relative emission intensity of the complex dissolved in piperidine decreased upon an increase of the temperature from 25 °C to 80 °C. This variation was measured at two exciting wavelengths (Table 1) corresponding to the β band (λ_{exc} = 530 nm) and γ band (λ_{exc} = 410 nm).
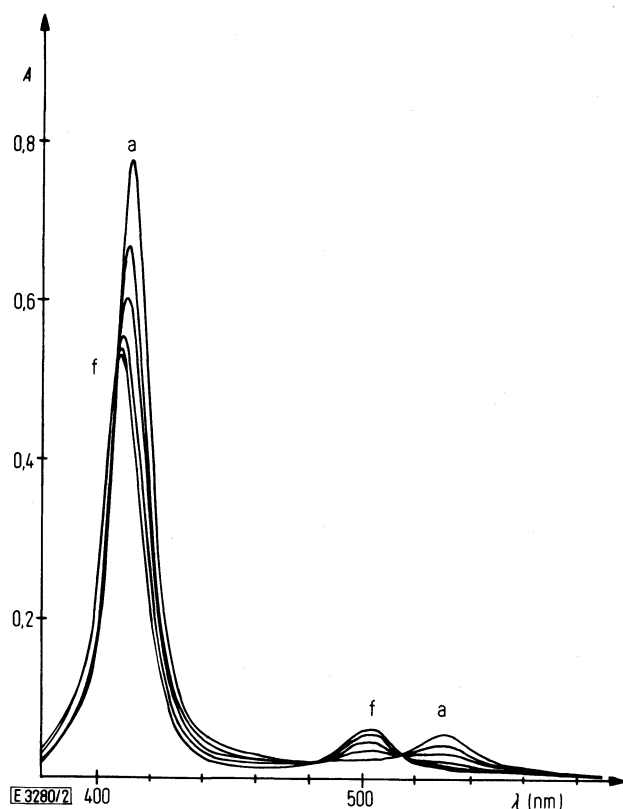

Fig. 2

Spectral changes during the photolysis of $2.89 \cdot 10^{-6}$ M (CO)(piperidine)(TPP)Ru(II), irradiating wavelengths > 380 nm. a: 0 min, b: 10 min, c: 20 min, d: 40 min, e: 80 min, f: 200 min irradiation time
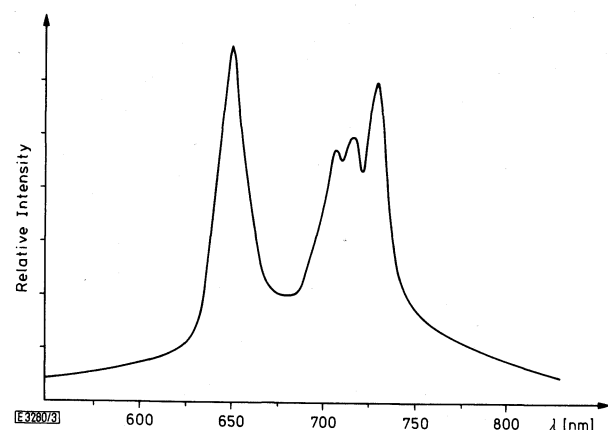

Fig. 3

Emission spectrum of solid (CO)(piperidine)(TPP)Ru(II) excitation wavelength: 406 nm, temperature: 77 K (relative intensity not corrected for multiplier response)

Discussion

(CO)(Piperidine)(TPP)Fe(II)

In the past it has been shown that a variety of hexacoordinated low-spin Fe(II) complexes of biological importance as CO-hemoglobin, CO-myoglobin, CO-hemochromogen, or CO-peroxidase which contain porphyrin, carbon monoxide and an additional base as ligands release the coordinated CO upon exposure to light [2]. The quantum yields of these reactions are rather high and may reach unity [6, 7]. The electronic spectra of these compounds exhibit, as far as investigated, only the characteristic absorption bands which have been assigned to spin-allowed $\pi\pi^*$ transitions of the porphyrin ligand [5]. Since the quantum yield of the photolysis which occurs upon light absorption of the porphyrin ligand was found to be independent of the irradiating wavelength [6, 7] one may assume that the lowest excited state of the porphyrin initiates the release of CO. However, it is difficult to understand how an excited state of the equatorial porphyrin ligand can lead to the substitution of the axial CO ligand.

Extensive studies of the emission spectra of porphyrin complexes have led to the rule that "the presence of excited states between the normal porphyrin triplet (which is the lowest excited state of porphyrin) and the ground state will quench the porphyrin phosphorescence" [24]. In other words the absence of porphyrin phosphorescence is an indication that the porphyrin singlets initially excited undergo a rapid radiationless transition to other excited states which lie below the lowest porphyrin triplet. This has been shown to occur in the case of a porphyrinytterbium(III) complex [25]. Light absorption by the porphyrin ligand leads to the emission of the rare earth metal. It follows that (CO) · (piperidine)(TPP)Fe(II) should emit phosphorescene of the porphyrin ligand if the porphyrin triplet is the lowest excited state of the complex. Since this compound is difficult to obtain in a pure state due to its instability and any emission may come from impurities, (piperidine)$_2$(TPP)Fe(II) which is a stable compound in the solid state and dissolved in piperidine was studied too. The electronic structure of both complexes should be similar as indicated by the similarity of the absorption spectra and by the observation that both have low-spin

ground states [15, 22]. There are only a few strong-field ligands which upon occupation of the axial ligand positions of tetraphenylporphine complexes of Fe(II) achieve spin pairing of the six d-electrons [23, 26]. It was found that upon light absorption into the α or β and γ bands neither the carbonyl nor the dipiperidine complex did emit any luminescence at temperatures down to 77 K. It follows that the porphyrin singlets initially excited are rapidly deactivated to an excited state which lies below the lowest porphyrin triplet. Consequently, it is not the porphyrin triplet but this lower excited state which is responsible for the photoreactivity of carbonylporphyrin complexes of Fe(II).

The most probable candidate for the reactive state is of the LF type. This has been suggested on the basis of a theoretical calculation [5]. In addition this assumption is also supported by the observation that the photochemistry of cyanide [8] and carbon monoxide [2] porphyrin complexes of Fe(II) is quite similar to that of $Fe(CN)_6^{4-}$ and $Fe(CN)_5CO^{3-}$ [9] as mentioned in the introduction. In analogy to cyanocobalamin [11], which has also a spin-paired d^6 ground state, it is assumed that the lowest LF triplet is the reactive excited state of carbonylporphyrin complexes of Fe(II). This LF triplet must then be populated with high efficiency as indicated by the large and wavelength-independent quantum yields of the release of CO.

However, while there is no reasonable alternative for a low-lying reactive state of cyanocobalamin the photolysis of carbonylporphyrins of Fe(II) may also be initiated by a CT state. Since Fe(II) is a reducing metal center and the porphyrin ligand has low-lying π* states, CT (dπ*) transitions are expected to occur at low energies [10]. Generally absorption bands of this type are quite intense. Although in addition to the porphyrin absorptions no other intense bands are present in the long-wavelengths region of the spectra of carbonylporphyrins of Fe(II) it is possible that they are obscured by the porphyrin bands. The complex (piperidine)₂ · (TPP)Fe(II) exhibits weak absorptions at longer wavelengths than the porphyrin bands. It has been suggested that these bands belong to CT (dπ*) transitions which are mixed with ππ* transitions of the porphyrin ligand by configuration interaction [23]. If such CT states of carbonylporphyrins of Fe(II) would have comparable or lower energies than the lowest intraligand π* states these CT states may be populated following light absorption by the porphyrin ligand. In such an excited state Fe(II) is oxidized to Fe(III). Since the strength of the π-accepting bond which accounts for the stability of metal-carbonyl bonds should decrease considerably if Fe(II) is oxidized to Fe(III) CT excitation may lead to the release of the CO ligand [9]. To our knowledge no carbonyl complexes of Fe(III) are known.

(CO)(Piperidine)(TPP)Ru(II)

The absorption spectrum of (CO)(piperidine)(TPP)Ru(II) exhibits only the characteristic ππ* bands of the porphyrin ligand. LF bands are certainly hidden under the intense porphyrin absorptions. In analogy to the iron complex [5] the long-wavelengths α and β bands are assigned to the first

excited singlet or Q state and the γ or Soret band at shorter wavelength to the second excited singlet or B state. Upon light absorption (CO)(piperidine)(TPP)Ru(II) showed the typical porphyrin phosphorescence and underwent a simultaneous substitution of CO. Our results suggest that the release of CO is initiated by an excited state which lies above the phosphorescing porphyrin triplet. It seems that the reactive state can be populated from the emitting one by thermal activation.

At 25°C the irradiation of the long-wavelengths α and β bands led to the appearance of the porphyrin phosphorescence and to the release of CO with a very low quantum yield. At 80°C the relative quantum yield of emission decreased but the quantum yield of photosubstitution increased significantly. It is assumed that the lowest excited porphyrin singlet undergoes intersystem crossing to the phosphorescing triplet. Increasing temperature leads to an increased population of the higher reactive LF state from the porphyrin triplet by thermal activation.

A decrease of the relative efficiency of emission and an increase of the quantum yield of CO release was again observed upon irradiation of the γ band at shorter wavelength. It follows that the second excited singlet undergoes also a radiationless transition to the lowest porphyrin triplet which can be deactivated by phosphorescence emission and by a thermally activated transition to the reactive LF state. However, at 25°C the quantum yield of CO release was much higher upon irradiation of the γ band than that which was obtained upon irradiation of the α and β band at longer wavelengths. This observation suggests that the photolysis which occurs upon irradiation at shorter wavelengths is not only caused by the thermally activated process. It is assumed that the energy of the second singlet is high enough that the deactivation cascade includes the population of the reactive LF state before the excitation energy finally reaches the lowest porphyrin triplet. The photochemical reaction must be fast enough to compete with other radiationless deactivations of the reactive LF state. A similar mechanism has been recently suggested to apply to the photolysis of Ir(phen)₂Cl₂⁺ [27].

Contrary to (CO)(piperidine)(TPP)Fe(II) the reactive excited state of the corresponding Ru(II) complex lies apparently above the lowest porphyrin triplet. This behavior is consistent with the assumption that the photolysis of both complexes is initiated by the lowest excited LF state. Due to the larger LF splitting of the heavier ruthenium the lowest excited LF state of (CO)(piperidine)(TPP)Ru(II) is expected to lie at higher energies than that of the corresponding Fe(II) complex. However, it is again not possible to exclude an excited CT (dπ*) state as the reactive state of (CO)(piperidine)(TPP)Ru(II). Substitution of Fe(II) by Ru(II) does not only lead to an increase of the energy of the LF transitions but the energy of CT (dπ*) transitions may increase too. In the case of the hexacyanides [28] and trisbipyridine complexes [29] the low-energy CT bands are shifted to larger wavenumbers by approximately 3000 cm⁻¹, if Fe(II) is replaced by Ru(II).

Regardless whether the reactive state is of the LF or CT type our interpretation is based of the assumption that the observed temperature dependence of the quantum yields of

emission and substitution is due only to the thermally activated population of the reactive LF state. But other excited state processes and particularly secondary chemical reactions as cage recombinations following the primary photochemical step may be temperature dependent too. However, the observation, that the quantum yield of CO release was dependent on the irradiating wavelength, strongly supports our suggestion that the reactive excited state can not be the phosphorescing porphyrin triplet.

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