

Tetrabenzporphyrin Complexes of Iron, Palladium and Platinum

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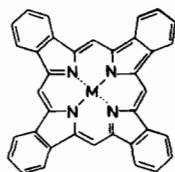
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The syntheses and absorption spectra of Fe(II)-TBP(pyridine)₂, Pd(II)TBP, and Pt(II)TBP (TBP = Tetrabenzporphyrin) are reported. The emission spectra of PdTBP and PtTBP were measured. Both complexes exhibit only phosphorescence from the lowest triplet of TBP. The Fe complex was oxidized to the cation [FeTBP(pyridine)₂]⁺ which was characterized by its absorption and ESR spectrum. The emission spectra of Pd and PtTBP as well as the spectral properties of [FeTBP(pyridine)₂]⁺ are discussed.

Introduction

Metalloporphyrins play a central role in many important biological processes [1, 2]. These include photosynthesis, redox reactions, and oxygen transport and storage. A particularly useful approach to learn more about these systems involves the substitution of the naturally occurring metals by others [3, 4]. The accompanying change of chemical and physical properties helps to clarify the role of the natural metalloporphyrins. A related approach is the modification of the porphyrin ligand. Tetrabenzporphyrin (TBP) appears to be a good choice for such investigations because, due to the extended π electron system, it deviates from natural porphyrins to the largest extent with respect to redox [5] and optical properties [6, 7]. Metal complexes of TBP were first



synthesized by Helberger *et al.* [8, 9] in 1938 and later by Linstead and his group [10, 11]. The metals include Mg, Zn, Fe, Cu and Mn. Later Cd, V, and Pd complexes of TBP were mentioned [12]. Although the initial spectroscopic studies showed that TBP complexes have unique optical properties [13], the investigation of these compounds was hampered by the difficulties encountered in the preparation of TBP

[6]. Only recently was ZnTBP prepared in high yield using a very simple template synthesis [14]. TBP proved to have very interesting redox properties [5].

We report mainly on the preparation of TBP complexes of Fe, Pd, and Pt. The description of the iron complex includes some observations on the redox behavior which is of interest with regard to the biological function of cytochromes. PdTBP and PtTBP were prepared in order to obtain some basic information on the optical properties of these complexes. The luminescence behavior, in particular, may give more insight into excited state processes of metalloporphyrins [7].

Experimental

Materials

Dipyridinetetrabenzporphyriniron(II)

To a solution of 10 g acetophenone-2-carboxylic acid (Aldrich) and 10 g ammonium acetate in 40 ml conc. ammonia in a 1 l flask were added 6 g iron powder and 4 g of molecular sieve (4 Å, Merck). The mixture was heated rapidly under a stream of nitrogen. Rapid heating was achieved by transferring the flask and contents to a fully pre-heated mantle. The temperature of the reaction mixture reached about 400 °C. After about 80 min the residue was allowed to cool with continued passage of N₂, washed with CHCl₃, and then extracted several times with hot pyridine. The combined extracts were cooled, added to ether, and filtered after 30 min. The dark-green filtrate was concentrated to 15 ml in a rotating evaporator. Upon addition of 30 ml ether the solution was chromatographed on Al₂O₃ (neutral), using a 20% solution of pyridine in ether as eluent.

The yellow-green fraction eluting first was discarded. The remaining eluate was concentrated to 5 ml by evaporation, treated with 50 ml methanol, and then allowed to stand overnight at -20 °C. The precipitate which formed was filtered off, washed with methanol and petroleum ether, and finally dried. The yield of almost black crystals of FeTBP(pyridine)₂ was 1.3 g (15%). *Anal.* Calcd: C, 76.46; H, 4.18; N,

11.63; Fe 7.73. Found: C, 76.33; H, 4.24; N, 11.57; Fe, 7.86.

The absorption spectrum of FeTBP(pyridine)₂ in pyridine/ether (1:5) shows band maxima at 596 nm ($\epsilon = 72000$), 573 nm (18500), 551 nm (12500), 428 nm (105000), 405 nm (48000), and 383 nm (73000). These bands agree fairly well with the spectrum reported by Linstead [10].

Free-base tetrabenzporphyrin

Crude ZnTBP [14] was not purified by chromatography but directly demetallated with concentrated sulfuric acid according to the method of Helberger [8]. The procedure applied by Linstead [10, 11] does not seem to offer any advantage. 2 g crude ZnTBP was stirred in 200 ml conc. H₂SO₄ at 40 °C for 30 minutes. The resulting greenish-brown solution was filtered. The filtrate was poured on 400 g crushed ice. After 12 hr the suspension was centrifuged at 6000 revolutions per minute for 15 min. The precipitate was washed with water and again centrifuged. This procedure was repeated until the water was free of acid. The precipitate was washed with acetone and dried at 80 °C. The yield of shiny dark violet crystals of TBPH₂ was 1.55 g (87%).

The absorption spectrum of TBPH₂ agreed well with that reported in the literature [15].

Tetrabenzporphyrinpalladium(II)

0.67 g TBPH₂ and 1.25 g PdCl₂ were dissolved in 85 ml dimethylformamide and stirred at 115 °C for 3 to 4 days. The reaction is completed when the absorption spectrum of TBPH₂ has been changed to that of PdTBP (see below). After evaporation the blue-black powder was dried and extracted with methanol overnight to remove excess PdCl₂. Additional impurities were removed by sublimation at 280 °C and 6 × 10⁻³ Torr. The residue was dissolved in DMF. The volume was reduced by evaporation. After precipitation with methanol the resulting suspension was kept overnight at -20 °C. The blue-black crystals of PdTBP were filtrated and dried at 80 °C (yield 0.5 g, 62%). *Anal.* Calcd: C, 70.30; N, 9.10; H, 3.28; Pd, 17.32. Found: C, 69.89; N, 9.06; H, 3.38; Pd, 17.67.

Tetrabenzporphyrinplatinum(II)

1 g platinum black was stirred in 10 ml Br₂ for 4 hr at room temperature. After addition of 5 ml ethanol, a solution of 0.3 g TBPH₂ in 75 ml dimethylformamide was added. This mixture was stirred at 110 °C for about one day until the spectrum indicated that TBPH₂ (absorption at 663 nm) was consumed. After evaporation the residue was extracted with methanol for 24 hr to remove an excess of PtBr₂. The product was first dried at 150 °C and finally at 220 °C in vacuum (6 × 10⁻³ Torr), to remove volatile impurities. The residue consisted

of shiny black-green crystals of PtTBP (yield 0.3 g, 73%). *Anal.* Calcd: C, 61.40; N, 7.96; H, 2.86; Pt, 27.78. Found: C, 61.11; N, 8.09; H, 3.74; Pt, 27.06.

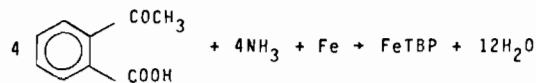
Spectra

Visible and ultraviolet spectra were measured with a Super Scan 3 spectrophotometer (Varian/Techtron). Solvents were spectrograde (Uvasole, Merck). Emission spectra were recorded on a modified Aminco spektrof luorometer SPF, equipped with a red-sensitive photomultiplier R 666 S (Hamamatsu). Additional cut-off filters were used to eliminate exciting light at the detector. ESR-spectra were measured with a Bruker ER 420 spectrometer (microwave frequency 9.5 GHz).

Results and Discussion

Dipyridinetetrabenzporphyrin

For the preparation of FeTBP the best results were not obtained by the metalation of the free base TBPH₂ [16] (see below) but by a direct modified template synthesis which has been successful for the preparation of ZnTBP [14]. Metallic iron as a powder reacts directly with commercially available acetophenone-2-carboxylic acid and ammonia at higher temperatures according to the stoichiometry.



FeTBP was not further investigated. Upon dissolution in pyridine, FeTBP(pyridine)₂ was obtained.

In solutions of methanol/pyridine (5:1) or ether/pyridine (5:1) FeTBP(py)₂ was oxidized by a variety of agents such as Cl₂, Br₂, I₂ or chloramine T. This oxidation is reversible. Upon reduction with NaBH₄ the oxidized complex was completely converted back to FeTBP(py)₂. The spectral changes accompanying this oxidation are shown in Fig. 1. The Soret band, although shifted and broadened, is still preserved while in the longer wavelength region the α -band of FeTBP(py)₂ almost disappears. Some less pronounced new absorptions occur. The spectral pattern of the oxidized complex is similar, although not identical, to that of low-spin hexacoordinated Fe(III) porphyrins [7]. The oxidation product may then be formulated as [Fe(III)TBP(py)₂]⁺. This is supported by the spectrum of [Zn(TBP⁺)][⊕] [5] and [Fe(II)(TBP[⊕])(py)CO]⁺ [17] which are clearly different from that of [FeTBP(py)₂]⁺. In the oxidation of Fe(II)TBP(py)CO, the TBP ligand is oxidized to the TBP π radical cation and the metal is not oxidized. This difference in oxidation behavior between the carbonyl and dipyridine complex can be explained by the larger stabilization of Fe(II) by CO

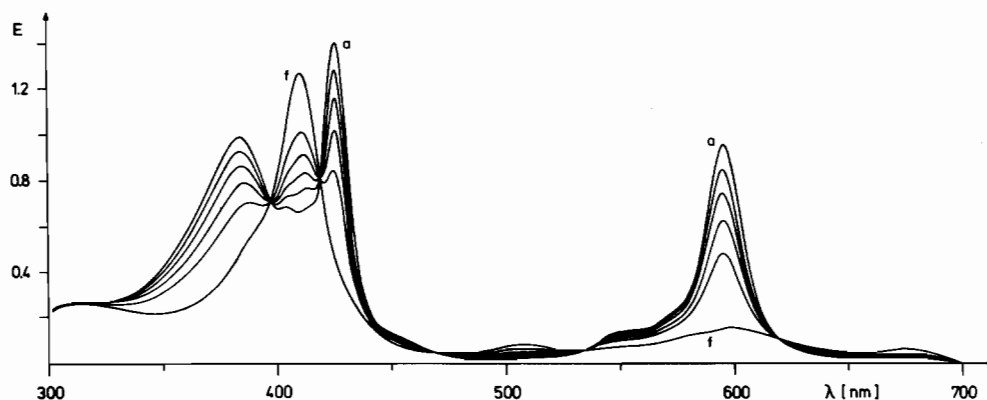


Fig. 1. Spectral changes during the oxidation of $1.34 \times 10^{-5} M$ FeTBP(pyridine)₂ by iodine in pyridine/methanol (1:10); 1 cm cell.

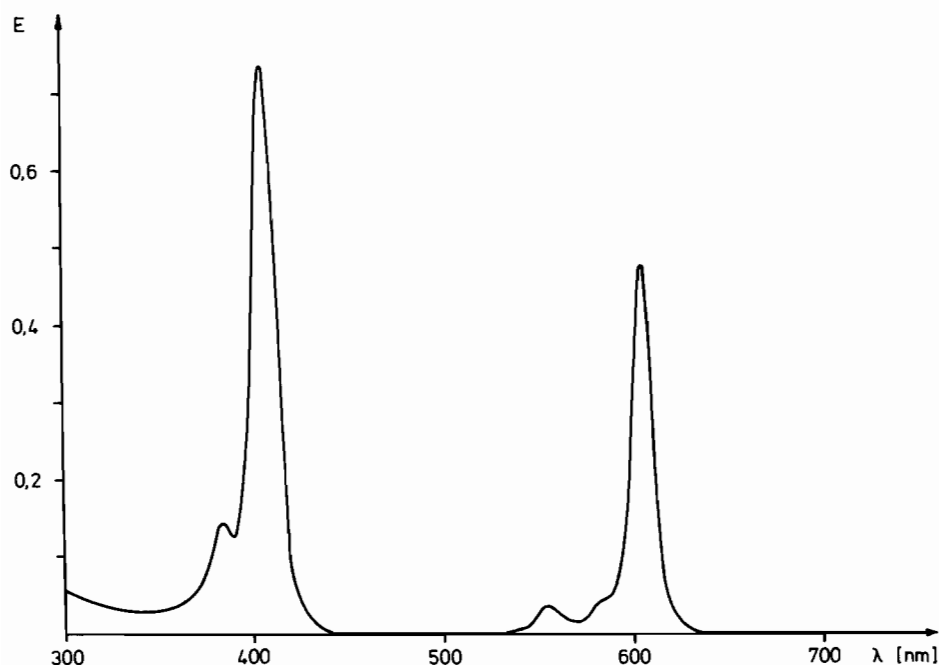


Fig. 2. Absorption spectrum of $4.1 \times 10^{-6} M$ PdTBP in DMF; 1 cm cell.

versus pyridine [17]. While in the carbonyl complex Fe(II) would be oxidized at higher potentials than TBP, Fe(II) is oxidized at lower potentials in the dipyrindine complex.

On the other hand, ESR spectra of [FeTBP(py)₂]⁺, which were obtained at temperatures between 45 and 77 K, do not indicate the formation of Fe(III). In contrast to ESR spectra of Fe(III) porphyrins [18] the spectrum of [FeTBP(py)₂]⁺ shows only a singlet with $g = 2.0018$ and a width of 3.75 G. This is similar to the spectra of [ZnTBP]⁺ [5] and [Fe(II)(TBP⁺)(py)(CO)]⁺ [17] where it has been shown that TBP was oxidized. Consequently the oxidation product of FeTBP(py)₂ should be formulated as [Fe(II)(TBP⁺)(py)₂]⁺.

Although these results on the optical and ESR spectra of [FeTBP(py)₂]⁺ seem to be contradictory and merit further investigation, a tentative explanation may be given. If the energy of [Fe(II)(TBP⁺)(py)₂]⁺ is only slightly lower than that of [Fe(III)-TBP(py)₂]⁺, (which is then actually a charge transfer excited state of the former) a temperature dependent equilibrium between both 'oxidation state isomers' [19] may exist. At low temperatures [Fe(TBP⁺)(py)₂]⁺ may prevail consistent with the ESR spectra. At room temperature the CT state may be populated in accordance with the optical spectrum. Since the ESR signal disappears above 77 K careful measurements of the temperature dependence of the absorption spectrum may give a definite answer. First

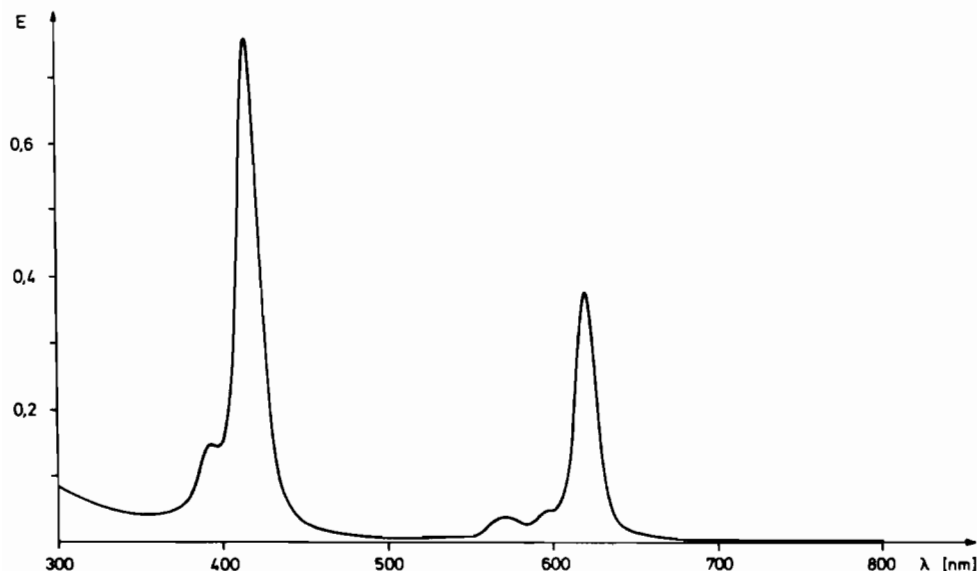


Fig. 3. Absorption spectrum of 3.56×10^{-6} M PtTBP in DMF; 1 cm cell.

TABLE I. Absorption and Emission Maxima (nm).

Compound	Absorption (ϵ); in DMF					Emission at 77 K, $\lambda_{exc.}$ 406 nm	
	B		Q			Solvent	T_1 (0, 0)
	Soret (0, 0)	other	α (0, 0)	others			
PdTBP	407 (179000)	384 (39300)	607 (105000)	584 (8700)	558 (6500)	DMF	762
PtTBP	416 (213400)	393 (45600)	621 (103200)	598 (12900)	571 (9400)	DMSO/Ethanol (1:1)	785

attempts to solve this problem failed due to inappropriate equipment.

Tetrabenzporphyrinpalladium(II) and Platinum(II)

The synthesis of PdTBP and PtTBP was achieved by the metalation of free base TBPH₂ by PdCl₂ and PtBr₂ in dimethylformamide. The progress of the reaction was conveniently followed by spectrophotometry. Attempts to metalate TBPH₂ by PdCl₄²⁻ and PtCl₄²⁻ or the benzonitrile complexes Pd(C₆H₅CN)₂Cl₂ and Pt(C₆H₅CN)₂Cl₂ [16] led to a mixture of products which could not be separated by chromatography. PdTBP and PtTBP sublime in a vacuum at higher temperatures.

The absorption spectra of PdTBP and PtTBP (Table I) are shown in Figs. 2 and 3. While for other porphyrins the Q and B bands are blue shifted on going from Pd to Pt, indicating an increase of back bonding [7], a red shift is observed for TBP. The spectrum of PtTBP seems to be almost 'regular' in

the terminology of Gouterman [7], since it is very similar to that of ZnTBP [6].

ZnTBP is unique in its emission behavior because it shows a fluorescence from the second excited singlet ($S_2 \rightarrow S_0$) in addition to the phosphorescence ($T_1 \rightarrow S_0$) and the normal fluorescence ($S_1 \rightarrow S_0$) [7, 12, 20]. The occurrence of this S_2 fluorescence is probably due to the large energy gap between the S_1 (or Q) state and the S_2 (or B) state. The S_2 fluorescence is very short living and was not quenched in CdTBP [12]. Cd increases intersystem crossing by its heavy atom effect. In contrast, the quantum yield of the longer living S_1 fluorescence of ZnTBP was greatly diminished in CdTBP. It thus was of interest to determine how transition metals with partly filled d-shells would affect the luminescence behavior of TBP. Although it has been mentioned that TBP complexes of Cu, V, and Pd do not emit the S_2 fluorescence no further data on the absorption and emission spectra of these complexes were reported [12].

PdTBP and PtTBP showed a normal emission behavior of the lowest excited states S_1 and T_1 , quite analogous to that of other Pd and Pt porphyrins [7, 21]. While the S_1 fluorescence was completely absent due to rapid intersystem crossing induced by the heavy metals, the normal phosphorescence ($T_1 \rightarrow S_0$) was observed at 77 K (Table I). It was, however, quite weak for PtTBP.

We were not able to detect any S_2 fluorescence [22] of PdTBP and PtTBP in accordance with the earlier observation on PdTBP [12]. For the palladium complex it has been suggested that the S_2 fluorescence is not quenched by the heavy atom effect but by the interference of ligand field states [12], which lie between the first and second excited singlets of TBP. The large energy gap between S_1 and S_2 of TBP, which is the origin of the occurrence of the S_2 fluorescence, may thus be bridged by ligand field states. The intervening LF states could be rapidly populated from S_2 of TBP.

Besides the $\pi\pi^*$ absorptions of TBP other bands have not been identified in the spectra of Pd and PtTBP. However, it seems doubtful if ligand field excited states of these complexes do occur below S_2 of TBP. The lowest ligand field transition ($^1A_{1g} \rightarrow ^3E_g, ^3A_{2g}$) of $Pt(NH_3)_4^{2+}$, which may be taken for comparison, gives rise to an absorption band at 286 nm [23]. Alternatively, the S_2 fluorescence may be quenched by the presence of lower-lying charge transfer (M to π^* TBP) excited states. Charge transfer (M to π^* ligand) transitions of bipyridyl and *o*-phenanthroline complexes of Pt(II) do occur at reasonable low energies [24, 25].

Acknowledgement

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