Preparation and Spectroscopic Properties of Pure Tetrabenzopor-phyrins
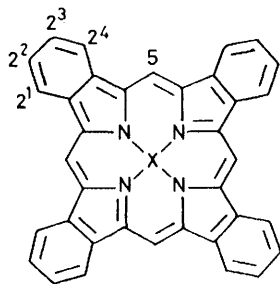
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Cadmium tetrabenzoporphyrin, tetrabenzoporphyrin, and the bispyridine complex of magnesium tetrabenzoporphyrin were synthesized. As judged from the visible absorption spectra these compounds are not contaminated with porphyrin-like impurities. 100-MHz ^{1}H Fourier-transform n.m.r. spectra of the above mentioned compounds are presented. From the low-temperature e.s.r. spectra it can be concluded that the lowest triplet state of biligated magnesium tetrabenzoporphyrin exhibits a static Jahn–Teller distortion resulting in a loss of four-fold molecular symmetry.

TETRABENZOPORPHYRINS form a class of stable compounds with attractive properties as models for naturally occurring tetrapyrrole derivatives. In the course of an investigation of the synthesis and spectroscopy of model compounds for chlorophyll and other photosynthetic pigments,[1] magnesium tetrabenzoporphyrin turned out to be more stable to photoinduced loss of magnesium than magnesium porphyrins without benzo-groups. Unfortunately, standard methods for synthesizing and

(I) X = Mg
(II) X = Cd
(III) X = 2H

purifying metallobenzoporphyrins result in products containing a persistent, non-negligible amount of impurities very similar to the main product [2] and so far no satisfactory methods have been reported by which these compounds can be freed from these impurities.

Spectroscopic data of the metallobenzoporphyrins indicate that the benzo-groups appear to have no appreciable electronic interaction with the porphyrin moiety. In this paper we report the preparation and purification of spectroscopically pure metallobenzoporphyrins, *i.e.* MgTBP (I), CdTBP (II), and the free base tetrabenzoporphyrin H$_2$TBP (III).

RESULTS AND DISCUSSION

Recently, Edwards *et al.* reported the synthesis of zinc tetrabenzoporphyrin by reacting a mixture of zinc acetate dihydrate and 3-carboxymethylphthalimidine at elevated temperature.[2] The visible spectrum of the product indicated the presence of an impurity with an absorption band at 460 nm, tentatively ascribed to a partly hydrogenated zinc tetrabenzoporphyrin.

To prepare (II) an intimate mixture of 2-carboxymethylphthalimidine and an excess of cadmium acetate dihydrate was heated under nitrogen for several hours. The mixture was successively extracted with light petroleum ether, benzene, and pyridine. The deep green extract obtained with pyridine was concentrated; when light petroleum was added, crude (II) precipitated. This material was purified by column chromatography. The CdTBP thus obtained is not contaminated by detectable quantities of porphyrin-like impurities as is shown by the visible absorption spectra. Further purification was achieved by heating CdTBP up to 350 °C at low pressure. A small quantity of unidentified material sublimed and the residue was found to be analytically pure (II). Several methods for demetallation of metalloporphyrins are known.[3] Attempts to convert (II) into (III) by acids such as hydrogen chloride and sulphuric acid failed; only a small quantity of rather impure (III) was obtained. However, carrying out the demetallation by treatment of a suspension of (II) in chloroform with an excess of trifluoroacetic acid at room temperature [4] gave dark blue crystals of (III) in high yield. This compound has a high degree of purity, as shown by its visible absorption spectrum, and could easily be purified to analytically pure (III).

Formation of (I) from (III) has been carried out employing hexapyridinemagnesium di-iodide.[5] As this reaction takes place in the presence of an excess of pyridine, the biligated complex of (I) with pyridine is formed.

Figures 1a and b present absorption spectra of (I) and (III) in THF containing pyridine (5%). The relevant wavelengths of all pure compounds including (II) have been collected in Table 1. If (II) is impure, it exhibits additional absorption bands at 460 and 640—650 nm and an impurity fluorescence band at 650 nm.

Figure 2 presents the ^{1}H (100 MHz) n.m.r. spectrum of (I). The relevant data of (I)—(III) have been collected in Table 2 and agree with those found from a less

TABLE 1

Visible absorption maxima of (I)—(III) in tetrahydrofuran containing 5% pyridine.

Compound									
(I)	$\lambda_{max.}/nm$	408	433	583	628				
	$\log \epsilon$	4.63	5.52	4.03	5.10				
(II)	$\lambda_{max.}/nm$	408	434	582	628				
	$\log \epsilon$	4.41	5.70	4.25	5.21				
(III)	$\lambda_{max.}/nm$	385	412	427	565	596	604	611	662
	$\log \epsilon$	4.11	4.87	4.93	3.49	4.34	4.26	4.07	4.20

resolved spectrum of the zinc compound.[6] Without decoupling, the ^1H resonances consist of two double doublets and one singlet, being assigned as indicated in
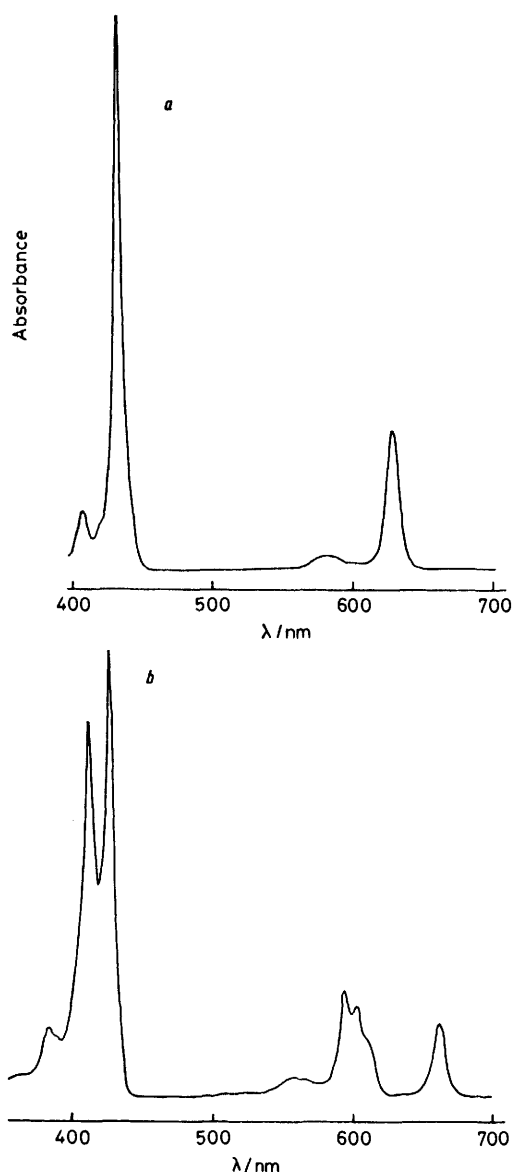

FIGURE 1   Visible absorption spectra of *a*, (I) and *b*, (III)

Table 2. By decoupling at δ 9.9, the H(2²) and H(2³) resonances are observed as a singlet.

Planar metallobenzoporphyrins have D_{4h} symmetry. Because of considerable strain in the benzopyrrole

moiety, the benzo-group is tilted by at least 20° with respect to the pyrrole plane, lowering the symmetry of the porphyrin to S_4 or D_{2d}. Both point-groups contain a degenerate representation for excited states. Thus, we should expect compounds (I) and (II) to exhibit a Jahn–Teller distortion, *e.g.* in the lowest excited triplet state T_0, observable by e.s.r.
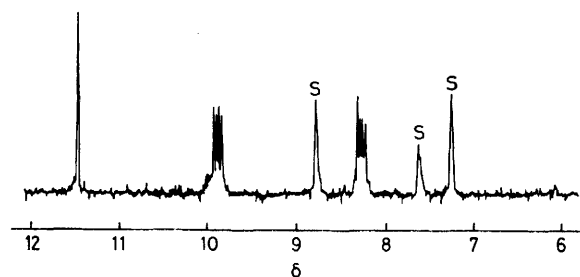
FIGURE 2   100-MHz ^1H N.m.r. spectrum of (I).   Peaks marked with S result from solvents

In a low-symmetry site of an organic glass [*e.g.* 2-methyltetrahydrofuran (MTHF), used in our experiments] the energies of the two electronic components of T_0 will be different by an amount Δ, defining the crystal-field splitting (see Figure 3). Usually, its value [7] is of the order of 10—100 cm⁻¹. At low temperatures, when $kT \ll \Delta$, only the lower electronic component of T_0 is populated, giving rise to an e.s.r. spectrum characteristic

TABLE 2

Proton chemical shifts (δ) of (I)—(III) [a]

	Compound			
Proton	(I) [b]	(II) [c]	(III) [d]	
H(2¹), H(2⁴)	9.8	9.9	9.7	Double doublet
H(2²), H(2³)	8.2	8.3	8.6	Double doublet
H(5)	11.4	11.2	11.3	Singlet
NH + CF_3CO_2H			11.1—	Singlet
			11.2	

[a] Using Me_4Si as standard. [b] Solvent: [²H₅]pyridine.
[c] Solvent: [²H₆]DMSO. [d] Solvent: $CDCl_3$ + trace CF_3CO_2D.
Coupling constants: $J_{13} = J_{24} \approx 2.5$ Hz; $J_{12} = J_{34} \approx 5.1$ Hz.

for a metalloporphyrin, for which the two mutually perpendicular in-plane axes (x and y) of the metalloporphyrin are non-equivalent and correspond to *different* values of the resonance field. The resulting e.s.r. spectrum, then, is that of a metalloporphyrin, subject to a static distortion to lower than four-fold symmetry.[7] At temperatures where $kT \gg \Delta$, however, rapid spontaneous transitions occur between both electronic components of T_0, during which the triplet spin quantum number ($m_s = \pm 1$, 0) is conserved, but the axes x and

y are interchanged (see Figure 3). Under these conditions, the observed e.s.r. spectrum is an average between both statically distorted geometries, and corresponds to an apparent four-fold symmetry again. This implies that the two separate resonances, corresponding to the

as well as H_x^- and H_y^-, have merged into single resonances $H_{x,y}^+$ and $H_{x,y}^-$, respectively, demonstrating the averaging between the aforementioned electronic components of T_0.

The spectrum of Figure 4b is that of a slowly cooled

TABLE 3

Zero-field splitting parameters of (I) and (III)

Species	Medium [b]	T/K	$10^4D/cm^{-1}$	$10^4E/cm^{-1}$	Experimental conditions
MgTBP·L [a]	MTHF–py (20 : 1)	15	341 ± 5	69 ± 5	Rapidly frozen solution
MgTBP·L$_2$ [a]		9	341 ± 2	37 ± 2	Slowly frozen solution
MgTBP [c]	PMMA	273	334 ± 3	0	Solid
H$_2$TBP [c]	MTHF–py (20 : 1)	15	194	44	

[a] L = pyridine (see text). [b] MTHF = 2-methyltetrahydrofuran; py = pyridine; PMMA = polymethylmethacrylate. [c] State of ligation unknown.

x and y axes of the metalloporphyrin at low temperature, merge into their average upon increasing the temperature. In terms of the zero-field splitting parameters D and E, defined in Figure 3, this can be stated to mean
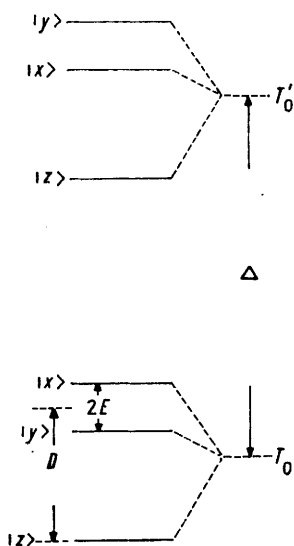

FIGURE 3 The two lowest triplet states T_0 and T_0' originating from an electronically degenerate triplet state in the presence of a crystal field Δ; $|x>$, $|y>$, and $|z>$ indicate triplet spin states in zero magnetic field. Assuming a negligible spin-orbital contribution to the zero-field splitting parameters D and E in T_0 and T_0', the splitting pattern in T_0 and T_0' is expected to be identical except for the interchange of $|x>$ and $|y>$. D and E are defined as indicated in this Figure

that at high temperature $E = 0$, whereas at low temperature $E \neq 0$.[7]

Figures 4a and b represent the $\Delta m_s = \pm 1$ triplet e.s.r. spectra of magnesium tetrabenzoporphyrin in polymethylmethacrylate (PMMA) plastic at 273 K, and dissolved in MTHF at 9 K in the presence of 5% pyridine. The form of both spectra is characteristic of a collection of randomly oriented triplets, as in an organic glass. From the resonance fields H_x^+, H_y^+, H_z^+, at high field and their low-field counterparts at H_x^-, H_y^-, and H_z^-, the zero-field parameters D and E of Figure 3 can be calculated straightforwardly, as indicated in Figure 4b. At 273 K (Figure 4a) the resonances at H_x^+ and H_y^+,

sample of MgTBP in MTHF–5% pyridine. At room temperature, the solution contains porphyrin both mono- and bi-ligated with solvent molecules (MTHF and/or pyridine) at the central Mg^{2+} ion.[1] Slow cooling displaces the equilibrium towards the biligated species: Figure 4b is thought to represent the $\Delta m_s = \pm 1$ triplet e.s.r. spectrum of (I) with two pyridine ligands.

Apart from that of the biligated species, a second triplet state of MgTBP (see Table 3) is also observed in rapidly frozen solutions, probably due to monoligated
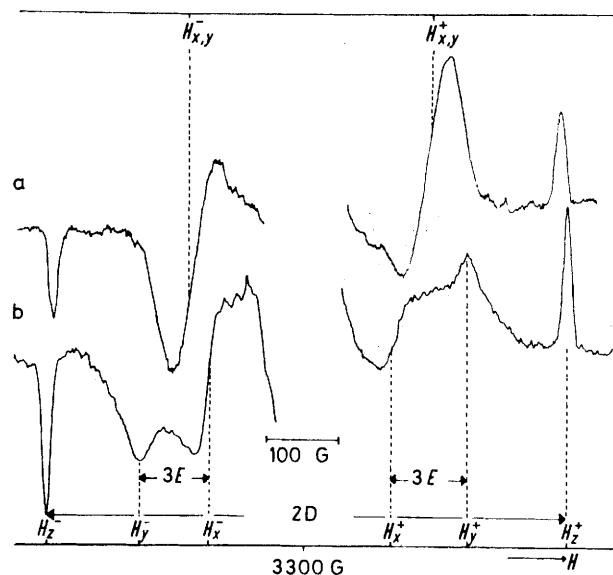

FIGURE 4 $\Delta m_s = \pm 1$ triplet e.s.r. spectra of (1). a, (I) in solid polymethylmethacrylate at 273 K; b, (I) in MTHF at 9 K, in the presence of 5% pyridine (slowly cooled sample). The change of solvent has no measurable effect on the results and can be ignored. Experimental conditions: microwave frequency, 9.1 GHz; microwave power a, 5 mW, b, 0.5 mW; field modulation frequency 100 kHz; modulation amplitude a, 16 G, b, 12.5 G. Spectrum b arises from biligated MgTBP, presumably with two pyridine molecules (see text). In both spectra the central region, containing a free-radical signal, has been omitted for reasons of clarity

MgTBP. This is confirmed by comparing low temperature fluorescence spectra of rapidly and slowly cooled solutions. The $\Delta m_s = \pm 1$ triplet e.s.r. spectrum of the second species also exhibits a temperature-dependent

Jahn–Teller distortion, and could be separately obtained by subtracting spectra of rapidly and slowly cooled solutions. In the concentration range 10^{-5}—10^{-3}M we did not observe a dependence of the relative amplitudes of both superimposed triplet e.s.r. spectra on concentration. Therefore, a dimerization equilibrium for both species, as invoked in a recent study of zinc and magnesium tetraphenylporphyrin,[8] seems unlikely. Although pyridine is expected to bind more strongly to MgTBP than MTHF, we cannot exclude that at low temperature MgTBP is partly ligated with MTHF due to the large excess of MTHF *versus* pyridine. In the centre parts of Figures 4a and b, a MgTBP$^+$ radical-ion signal has been omitted for reasons of clarity. These radical ions are irreversibly formed by illumination of solid solution of porphyrins at low temperature.

For CdTBP no triplets could be detected by conventional e.s.r. down to 5 K, presumably due to a very short triplet lifetime, resulting in a small steady-state triplet concentration under continuous illumination. Rapid deactivation of the lowest triplet state is expected to occur in CdTBP because of a strong spin–orbit coupling involving the heavy cadmium atom. For the free base H_2TBP in MTHF containing a small amount of pyridine in excess of H_2TBP at 15 K, triplets can be readily detected. Since the molecule has at most a two-fold symmetry there is no Jahn–Teller distortion, as described for MgTBP. Accordingly, the e.s.r. spectrum of (III) did not exhibit a temperature-dependent lineshape in the *xy* region, as observed for the magnesium compound.

EXPERIMENTAL

Visible absorption spectra were taken with a Shimadzu UV-200 double beam spectrophotometer. N.m.r. spectra were determined using a Varian Associates XL-100 Fourier-transform n.m.r. spectrometer.

E.s.r. measurements were carried out on a Varian E-6 spectrometer, equipped with a variable-temperature unit and a flow cryostat (Oxford Instruments) for the temperature range 4—300 K. Samples were rigid solutions of 10^{-3}—10^{-4}M-MgTBP in 2-methyltetrahydrofuran (MTHF) or in polymethylmethacrylate (PMMA). For the creation of photoexcited triplet states the samples were irradiated with $\lambda > 570$ nm light.

Cadmium Tetrabenzoporphyrin.—3-Carboxymethylphthalimidine was prepared according to the method described by Edwards *et al.*[2] 3-Carboxymethylphthalimidine (3.5 g, 18.3 mmol) and cadmium acetate dihydrate (3.2 g, 12.0 mmol; Merck p.a) were ground to a homogenous mixture which was placed in a test tube (2.5 × 20 cm) and heated to *ca.* 345 °C in a Wood's metal bath for 3.5 h, while nitrogen was passed through the tube. A total of 18.5 g (97 mmol) of 3-carboxymethylphthalimidine was treated this way. The melts were combined and extracted with distilled light petroleum (200 ml; b.p. 60—80 °C; 3 h), distilled benzene (200 ml; 4 h), and finally with pyridine (200 ml; 7 h; Merck p.a.). The hot pyridine solution was filtered, the filtrate was concentrated *in vacuo*, and then diluted with light petroleum (400 ml; b.p. 20—40 °C). After cooling to 0 °C the solution was filtered. A green product containing

CdTBP was collected (6.5 g). This material was chromatographed in three portions on a 2.5 × 50 cm column of alumina (ICN; activity I) using pyridine–diethyl ether (1 : 2.5) as eluant. The spectrally pure fractions were combined and the solvents were removed *in vacuo*, yielding blue-violet crystals of (II) (205 mg). Work-up of the impure fractions resulted in another 15 mg of (II) (total yield 220 mg = 0.35 mmol, 1.5%). This product was further purified by heating to 350 °C at 10^{-4} mmHg. The material which did not sublime was found to be analytically pure (Found: C, 69.75; H, 3.25. Calc. for $C_{36}H_{20}CdN_4$: C, 69.65; H, 3.25%).

Tetrabenzoporphyrin (III).—Pure (II) (100 mg, 0.16 mmol) was suspended in chloroform (5 ml) and trifluoroacetic acid (EGA; 99%; 2.5 ml) was added dropwise, yielding a deep blue-green solution. After stirring for 45 min at room temperature demetallation was complete, as shown by the visible absorption spectrum. The solution was poured into 50% aqueous ethanol (50 ml) and the mixture neutralized with solid sodium carbonate. The precipitate was isolated by filtration and washed well with water and ethanol. Compound (III) so prepared was contaminated with a solid impurity, presumably $Cd(OH)_2$, which was removed by boiling briefly in glacial acetic acid (25 ml). The product was then triturated with warm pyridine (2 ml) to remove traces of (II) and filtered. Final purification was effected by dissolving (III) in trifluoroacetic acid (5 ml), filtration through a sintered glass funnel, and precipitation of the product with distilled methanol (10 ml). The product was dried at 150 °C *in vacuo* for 24 h to give (III) (80 mg, 0.157 mmol, 97%) as dark-blue crystals (Found: C, 84.35; H, 3.9. Calc. for $C_{36}H_{22}N_4$: C, 84.7; H, 4.35%).

Bispyridine Complex of Magnesium Tetrabenzoporphyrin (I).—Hexapyridine magnesium di-iodide was prepared from magnesium turnings (300 mg), iodine (1.0 g), and dry pyridine (20 ml) according to the literature procedure.[5] Compound (III) (30 mg, 0.059 mmol) was added and the suspension heated to reflux for 7 h under nitrogen. The mixture was filtered from magnesium salts and the filtrate poured into water (50 ml). The precipitated (I) was collected by filtration and washed with water. Column chromatography (alumina, activity III–acetone) of the crude product followed by recrystallisation from pyridine–iso-octane and drying at room temperature *in vacuo* for 24 h gave (I) (20 mg, 0.029 mmol, 49%) as a deep blue-green solid (Found: C, 79.0; H, 4.1. Calc. for $C_{46}H_{30}MgN_6$: C, 79.95; H, 4.4%).

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