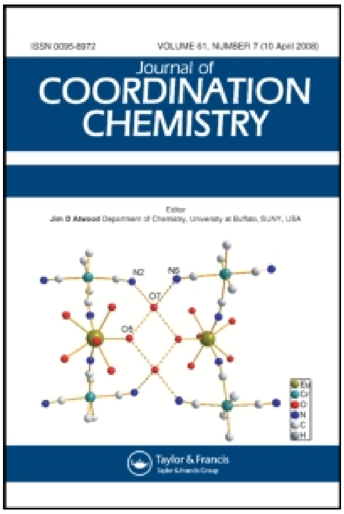

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UNUSUAL METALLOPORPHYRINS: SYNTHESIS AND PROPERTIES OF A DIMETALLIC BORON PORPHYRIN COMPLEX

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UNUSUAL METALLOPORPHYRINS: SYNTHESIS AND PROPERTIES OF A DIMETALLIC BORON PORPHYRIN COMPLEX

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Reaction of BCl_3 acetonitrile adduct with tetraphenylporphine affords the corresponding chloro-boron complex. Chromatography of this chelate on alumina results in ligand exchange producing an unusual tetrahydroxydiboron porphyrin. This complex is characterized by visible, ir, nmr, and mass spectrometry, as well as elemental analysis. The diboron derivatives are easily demetallated in solution and are formulated as having out of plane structures. These may be models for metal ion incorporation into porphyrins.

INTRODUCTION

The porphyrin complexes of all the group IIIA elements except boron have been synthesized and well characterized.[2–4, 12] Although a boron complex of octaethylporphyrin (OEP) has been reported (1964), further work has never subsequently appeared in the commonly available literature and the complex was never well characterized.[5] Such a complex might have interesting medical applications in the treatment of cancer by neuron capture therapy, due to the reported tumor localizing ability of several porphyrins[6] and the high cross section of boron for neutrons.[7] We report here the synthesis and properties of an unusual diboron complex of TPP. A probable structure of the boron porphyrin chelate is also proposed.

EXPERIMENTAL SECTION

Physical Measurements

Infrared spectra were recorded on a Beckman IR–8 spectrometer as KBr pellets. Mass spectra were obtained on a CEC21–110B mass spectrometer operated at 70 eV. Pmr spectra were recorded in $CDCl_3$ on a Varian HA–100 spectrometer using TMS as an internal standard. C^{13}-NMR spectra were obtained on a JEOL PS–100 ^{13}C pulsed Fourier transfer NMR spectrometer operating at 25 MHz with proton noise decoupling. Spectra were recorded in $CDCl_3$ solution and shifts are reported relative to TMS. Electronic spectra were run on either a Cary-14 or Beckman Model-24 spectrophotometer using 1 cm cells.

Reaction of Tetraphenylporphine with BCl_3

Into a three necked flask were placed 1 ml of reagent grade acetonitrile and 50 ml of dry chlorobenzene. Dry nitrogen was introduced through one neck and excited through a drying tube placed atop a condenser in the centre neck. BCl_3 was bubbled through an inlet tube in the third neck, with stirring, for about 30 min or until fuming above the inlet occurred. The $BCl_3 \cdot CH_3CN$ adduct precipitated out as a white material. 500 mg of tetraphenylporphine (TPP) was then added and the mixture was brought to reflux. The initially red solution turned green and was allowed to reflux for 24 hours. After this time the solution had darkened to a reddish green colour and the reaction was stopped. The flask was allowed to cool and then kept stoppered at 4°C for three days after which time violet crystals appeared. The product was filtered off, washed with benzene and dried to yield ~400 mg of product $\underline{I}$. Product $\underline{I}$ was was not characterized due to its pronounced insolubility and instability in organic solvents. The entire quantity of product $\underline{I}$ was then chromatographed on basic alumina using benzene and chloroform as eluants. The benzene elutes off a faint pink fraction that has been identified as TPP by its visible spectra. The chloroform (which contains ~1% ethanol to promote ligand exchange) elutes off a deep blue fraction of the desired product. The solution was evaporated and dried at reduced pressure to afford an almost quantitative yield (overall yield 70%) of tetrahydroxydiboron TPP (II), mp > 350°C. Calcd. for $C_{44}H_{32}N_4B_2O_4 \cdot \frac{1}{2}C_2H_5OH$:[8] C, 74.51; H, 4.86; N, 7.72; B, 2.98. Found: C, 74.70; H, 5.16; N, 7.26; B, 2.77.

λ_{max} (EtOH) 427 nm (117,000), 531 (2,600), 573 (10,100), 622 (10,500). Pmr($CDCl_3$) 1.05 ppm(m), 3.88(m), 7.78(m), 8.30(m), 8.64(s), 8.96(s) Ir(KBr) 3400 cm^{-1}, 2950, 2890, 1269, 1252, 1093, 1070, 760.

RESULTS AND DISCUSSION

PMR

The Pmr spectrum is fairly typical of TPP complexes except that the β-pyrrole protons are split into a doublet. The low intensity peaks observed at 1.05 and 3.88 ppm have tentatively been assigned to the methyl and methylene protons respectively of the ethanol of crystallization. A broad multiplet corresponding to 12 protons at 7.78 ppm represents the meta and para protons of the meso-phenyl groups. A multiplet at 8.30 ppm corresponds to 8 protons and is assigned to the ortho phenyl protons. Two sharp singlets at 8.64 and 8.96 ppm (4 protons apiece) are the β-pyrrole protons on the macrocyclic ring. The existence of two resonances for the β-pyrrole hydrogens indicates that the boron is asymmetrically coordinated to the porphyrin ring. Similar splittings have been observed in the highly asymmetrically coordinated H-Re$(CO)_3$TPP[9] and in TPP itself when the N–H tautomerism is frozen out.[10] In addition the resonances are at abnormally high field values (for metal TPP complexes) indicating some distortion of the porphyrin ring. Such a distortion would be expected to reduce the ring current and cause an upfield shift for β-pyrrole proton resonances. The values found are similar to those in the $H_4(TPyP)^{2+}$ and $H_4(TPP)^{2+}$ dications.[11] These are known to have highly distorted porphyrin rings with extensive ruffling, and to have the phenyl rings more nearly coplanar with the porphyrin macrocycle. Such enhanced coplanarity is expected to result in bathochromic shifts in the visible spectra of this compound due to increased resonance interaction between the two ring systems. It also may explain why there is no non-equivalence of the o-phenyl protons, as has been observed in many unsymmetrically coordinated metalloporphyrins. One final point to note is the failure to observe any signals corresponding to the hydroxyl hydrogens. This is not unexpected and appears to be the rule rather than the exception in hydroxy or aquo metalloporphyrins.[12]

C^{13}-nmr

The C^{13} spectrum for compound II was obtained. Due to relatively poor signal noise ratios and the apparent broadening of many of the resonances a completely satisfactory spectrum was not obtained and only partial assignments are attempted here. Assignments are based on comparison with free TPP and previously established metallo-TPP spectra.[13] The α-pyrrole carbon resonances are observed as a doublet at 147.8 and 147.0 ppm, indicating two different environments for these carbons. The α-pyrrole carbons are not observed in some free base porphyrins but are seen in the metallocomplexes presumably due to N–H tautomerism in the free base.[11] The β-carbon signals are broadened beyond observation in the boron complex as no resonance near 132 ppm is seen. We attribute this to B–N tautomerism in the metallocomplex with two distinct α-carbon sites frozen out while the β-carbon resonances are approaching coalescence. A similar phenomena has been observed in free base and N,N′-dideutero TPP, with an increasing coalescence temperature for the heavier isotope.[14] If this assignment is correct we can then assign a resonance at 142.0 as the C_1 of the phenyl ring and one at 128.2 as the C_3–C_3' carbons. A peak at 125.9 can be assigned as the C_4 phenyl carbon by comparison with known spectra. A complicated set of broad peaks with maxima at 137.3 and 135.1 ppm must be the C_2 and C_2' ortho carbons, which are apparently non-equivalent. Although we observe no clear non-equivalence in the H^1 nmr spectra, the o-hydrogen peak is broad and the shift differences are expected to be about twice as great in the C^{13} spectra.[13] The meso carbon peak is also broadened in the C^{13} spectra but is assigned at 123.3 ppm. The carbons for the ethanol of crystallization were not observed.

Visible Absorption Spectra

The electronic absorption spectra of II is shown in Fig. 1. Complex II gives a normal two banded spectrum and shows a bathochromatic shift compared to most other metalloporphyrins. A pronounced metal effect has been observed[15] in the monometallic group IIIA OEP complexes. Along this series there is a significant red shift and a decrease in the Q(0,0)/Q(1,0) intensity ratio. This trend appears to be

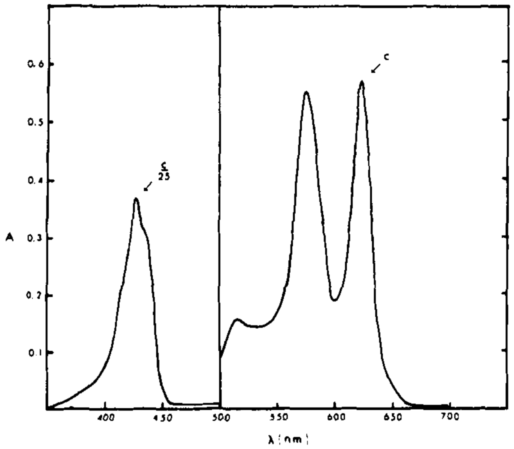


FIGURE 1 Visible absorption spectrum of compound II in ethanol. Concentration C is 5.4 x 10^{-5} M.

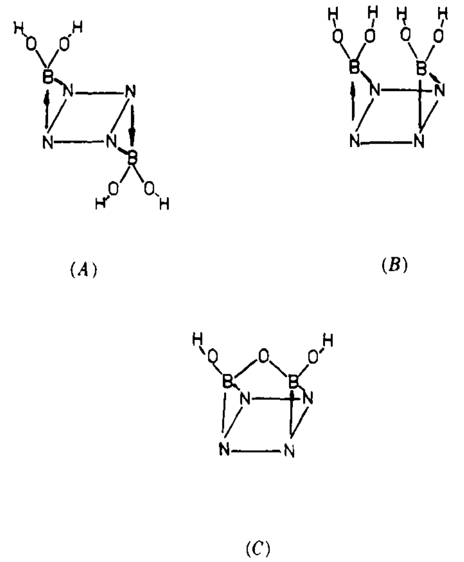
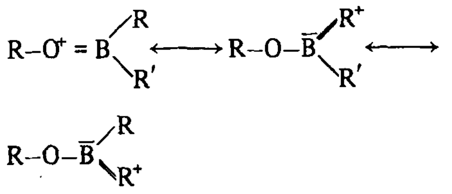


FIGURE 2 Possible structures for compound II. Structure (C) represents the structure proposed by Thomas for the OEP boron complex.

reversed for in dimetallic boron complex (II) (no mono boron complexes are known). The spectra of II is blue shifted and the Q(0,0)/Q(1,0) ratio is nearly equal to unity, opposite of what would be expected for the mono boron complex. The spectrum is very similar to that of the disodium and dilithium TPP complexes reported by Dorough *et al.*[16] This may be a consequence of highly ionic metal porphyrin bonds in II or of an out of plane position for the boron moiety.

Infrared Spectra

The ir spectrum of II shows new bands as indicated in the Experimental section. No strong bands are observed in the region between 1300–1400 cm^{-1} where normal B–O–B, B–O and B–N stretching modes are found. However, the presence of strong bands at 1003 and 1070 cm^{-1} and 1269 and 1252 cm^{-1} can be assigned to the $B\leftarrow N$ (dative bond) and B–O stretching respectively.[17] The decrease in frequency and intensity of the B–O stretching vibrations indicates no resonance interactions such as



$$R{-}O^{+}{=}B\begin{smallmatrix}R\\ R'\end{smallmatrix}\longleftrightarrow R{-}O{-}\bar{B}\begin{smallmatrix}R^{+}\\ R'\end{smallmatrix}\longleftrightarrow R{-}O{-}\bar{B}\begin{smallmatrix}R\\ R^{+}\end{smallmatrix}$$

are occurring, as the high frequency and intensity in normal boron complexes with unfilled octets have been attributed to such structures.[17] Resonance of this type is largely suppressed when these compounds are coupled to electron donors such as pyridine or other tertiary bases. Thus we conclude that the boron octet is being filled by one of the adjacent nitrogens of the porphyrin ring (as in Figure 2). This is further supported by the strong bands at ~ 1100 cm^{-1} which are indicative of $B\leftarrow N$ dative bonds. The normal B–N stretching bands may be overlapped with the B–O bands for the same reasons as already outlined. Finally a broad weak OH band can be seen at about 3400 cm^{-1}.

Mass Spectra

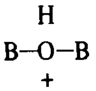
The use of mass spectra in porphyrin chemistry has been spurred by the usual stability of the molecular ion which is often the base peak facilitating determination of the molecular weight. However, Smith *et al.* have reported unusual mass spectral patterns for thallium (III) porphyrins where the demetallated ligand is the base peak.[18] In the boron porphyrin the parent molecular ion at m/e 702 is found but is weak (Table I). We observe that the demetallated ligand is an abundant peak but the doubly charged ion corresponding to $|B_2OHTPP|^{++}$ is the base peak, with other high abundance peaks corresponding to $|B_2OHTPP|^{+}$ and H_2TPP^{+}. Thomas reports a very stable $|B_2O$-porphyrin$|$ moiety in the mass spectra of the boron–OEP complex.[5] We observe a stable B_2OH moiety in the centre rather than a B_2O. Whether the H^{+} has been transferred from the axial ligands to the

TABLE I
Relative intensities of ion species of interest in the mass spectrum of II

m/e	Rel. abun.	Assignment
702	6	M^+
651	96	M^+–3 OH $\quad |B_2OHTPP|^+$
614	70	TPP^+
325.5	100	$|B_2OHTPP|^{2+}$
307	32	TPP^{2+}
Isotope peaks of parent ion		
m–2	.36	
m–1	.77	
m	1.00	
m+1	.44	
m+2	.13	

m = ion containing the most abundant isotopes of all elements present (assumed B^{11} ∿ 80%, B^{10} ∿ 20%).

macrocycle or is present as a



$$\overset{\displaystyle H}{\underset{+}{B{-}O{-}B}}$$

entity is unknown. Such proton transfers are known and in fact two protons must be transferred to the macrocycle to give the H_2TPP^+ ion. The directly demetallated ligand is also observed.

Demetallation of II

Complex II is demetallated slowly in ethanol by water, more rapidly by acetic acid and instantaneously by HCl/CH_2Cl_2. Thus it belongs to stability class V.[19]

Complex II is stable in pure dry methylene chloride but in CH_2Cl_2 containing a trace of acid the complex goes through a series of transformations with time which yield free TPP or H_4TPP^{2+} depending on the quantity of acid added. These transformations are similar in appearance to those reported by Smith *et al.* for HgTPP which they ascribe to the following reactions.[20]

$$2HgTPP + 2HCl \longrightarrow TPPH_2 + Cl{-}Hg{-}TPP{-}Hg{-}Cl$$

$$Cl{-}Hg{-}TPP{-}Hg{-}Cl + 2HCl \longrightarrow TPPH_2 + 2HgCl_2$$

Figure 3 shows the transformation with time of II into other species with λ_{max} 420 nm and 445 nm. We have identified these two species as H_2TPP and H_4TPP^{2+} by their characteristic visible spectra. An isobestic point is observed at 437 nm. In the presence of slightly more acid, Figure 4 is obtained where II has been directly demetallated into H_2TPP without detection of intermediates and is slowly converted into the diacid. A third intermediate (Figure 5) has also been detected by monitoring the reaction in the visible region (500–700 nm). Prior to formation of H_2TPP an additional specie is present, which is identified by its strong absorption at 498 nm, a position where neither H_2TPP, H_4TPP^{2+} nor II absorb. We believe this corresponds to III, the monometallic intermediate. Smith has proposed a dimetallic HgTPP complex as an intermediate in the demetallation of mercury tetraphenylporphine which decomposes to give a monochloro monomercury TPP derivative and ultimately to yield H_2TPP. Our results indicate a similar process, starting with the dimetallic boron complex. The demetallation of metal porphyrins is thought to proceed via protonation of the complex followed by loss of metal ion from the back side of the molecule.[21] Thus we may postulate a tentative mechanism for the demetallation of II.

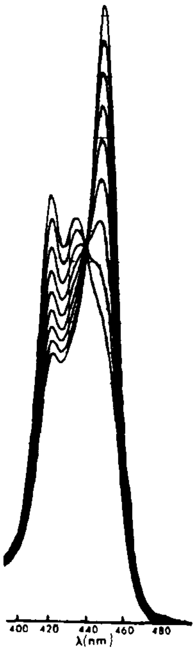


FIGURE 3 Repeated traces with time of the Soret region of the electronic absorption spectrum of complex II in CH_2Cl_2 containing a trace of hydrogen chloride.

FIGURE 4 Repeated traces with time of the Soret region of the electronic absorption spectrum of complex II in CH_2Cl_2 containing a slightly larger amount of hydrogen chloride (see text).

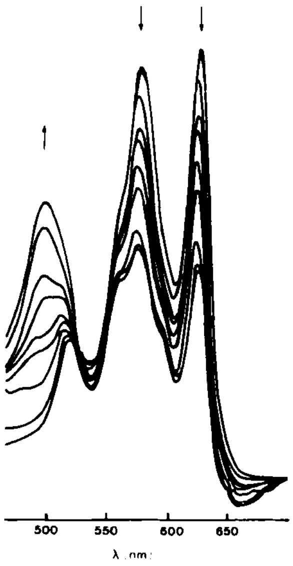
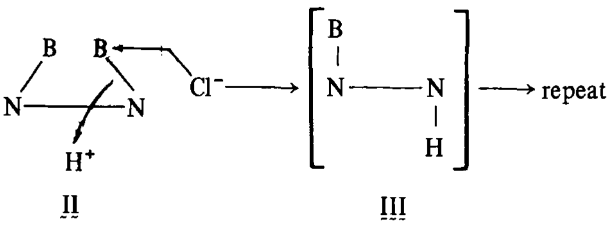


FIGURE 5 Repeated traces with time of the visible absorption spectra of complex II in CH_2Cl_2 containing a trace of hydrogen chloride.



$$H_2TPP \xrightarrow{2HCl} H_4TPP^{2+}$$

Thus the demetallation in acid proceeds through free H_2TPP and thence to the diacid. In very weakly acidic solutions an additional intermediate III can be detected. This is further evidence for the dimetallic intermediates proposed as models for metal ion insertion into porphyrins and is consistent with Smith's model for the demetallation of HgTPP.

Proposed Structure

Due to the protracted difficulties in obtaining a single crystal suitable for x-ray diffraction analysis, we feel justified in proposing a structure for II based on the extensive chemical and spectroscopic data. It is difficult to assign an exact structure but the nmr, mass spectra, and infrared analysis are consistent with a structure such as A or B. However, we cannot at this time rule out the alternative structures with absolute certainty.

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8. If highly dried and purified $CHCl_3$ (ethanol preservative removed) is used for the chromatography no product is found to elute until some ethanol is added. In addition the product II is unstable in pure $CHCl_3$ and decomposes rapidly unless ethanol is present. This data in addition to the elemental analysis and nmr lead us to propose ½ mole of ethanol of crystallization.

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