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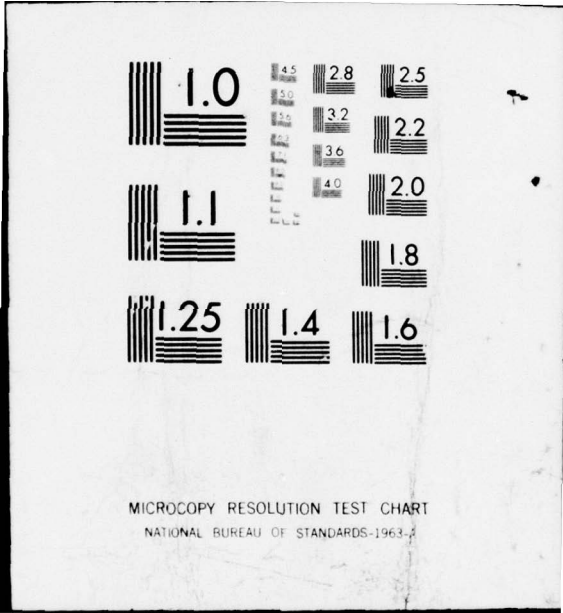UNCLASSIFIED   TR-16   NL

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Unusual Metalloporphyrins

Phosphorus Complexes of Tetraphenylporphine

by

Carl J. Carrano and Minoru Tsutsui

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The synthesis and spectral properties of several phosphorus complexes of tetraphenylporphine (TPP) are reported. The compounds appear to have the form $(TPP)P(V)X_2^+Y^-$ as previously reported by Gouterman et al. for the analogous octaethylporphyrin (OEP) complexes. The electronic and nmr spectra show a striking dependence on the nature of the anionic ligand X, which has not previously been reported and appears to be inconsistent with a symmetrical in-plane structure. $*(TPP)P(V)X(2+)Y(-)$

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Unusual Metalloporphyrins.

Phosphorus Complexes of Tetraphenylporphine

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Abstract: The synthesis and spectral properties of several phosphorus
complexes of tetraphenylporphine (TPP) are reported. The compounds
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and nmr spectra show a striking dependence on the nature of the anionic
ligand X, which has not previously been reported and appears to be incon-
sistent with a symmetrical in-plane structure.

Introduction:

Metalloporphyrin derivatives of the Group VA elements have recently been discovered.[1] Phosphorus complexes, in particular, of octaethylporphyrin (OEP) have only just been reported.[2] Independently we have prepared similar phosphorus complexes of tetraphenylporphine (TPP) that have shown some unexpected properties.

Interest in this class of porphyrins stems from the existence of two possible oxidation states, +III and +V for the central "metal". Recent evidence has shown that the valence +V species has the form $(P) M(V)X_2^+Y^-$, where (P) stands for a porphyrin, M for a group VA metal, X for an anionic ligand and Y for a non-ligand counter ion.[2] Theory has predicted and experiments have shown that, for OEP at least, the complex should have a "normal" optical absorption spectra. The formation of what appears to be mixed complexes where the two anionic ligands X are different has resulted in some interesting spectroscopic properties which are reported herein.

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 $CDCl_3$ or d^6-DMSO either on a Varian T-60 or HA-100 nmr spectrometer using TMS as an internal standard. Electronic spectra were run on either a Cary-14 or Beckman 24 spectrophotometer using 1 cm cells.

Reaction of Tetraphenylporphine with $POCl_3$

Into a 50 ml round bottom flask were placed 500 mg of tetraphenyl-

porphine (TPP) and 20 ml of reagent grade pyridine. Approximately 4 ml of $POCl_3$ were gradually added dropwise and the solution was refluxed for 24 hrs. The initially red solution turned a greenish-red and precipitated violet crystals. The reaction mixture was hydrolyzed by the dropwise addition of methanol until HCl evolution ceased. Additional methanol was added to bring the solution volume up to 40 ml. Dissolved HCl was removed by slight warming under reduced pressure. The solution was then filtered and 250 ml of acetone was added to the filtrate. On some occasions two layers were formed. The acetone solution was flash evaporated to yield the crude product. This was then chromatographed on basic alumina using benzene, chloroform and methanol as eluants. The benzene eluted a faint red fraction (TPP), the chloroform a dark red fraction (I), and the methanol a greenish-violet band which contained the bulk of product II. The solutions were evaporated to dryness and then fully dried at 100°C over P_2O_5 under vacuum. Only a small amount of product I was obtained and it was not fully characterized although a visible spectra was obtained. Product II analyzed to be TPP P(V) $OHCl^+$ Cl^-.

Calcd. for $C_{44}H_{29}N_4Cl_2PO \cdot 3H_2O$: C, 67.18; H, 4.61; N, 7.12; P, 3.93; Cl, 9.01.

Found: C, 67.83; H, 4.74; N, 7.24; P, 3.87; Cl, 9.35.

MW (ethanol), 342 (ionized) theoretical 732

λ_{max}(MeOH) 434 nm (280,000), 525 sh, 562 (17,000), 609 (6,000).

Pmr ($CDCl_3$) 2.40 ppm (s, H_2O), 7.58 (s, p-H) 7.75 (s, m-H), 7.92 (s, o-H), 8.90 (d, β-H), 9.16 (d, β-H).

IR (KBr) 1070 cm^{-1}, 1033, 1019, 895, 793, 752, 698, 680.

Reaction of II with Aqueous Pyridine:

Compound II could be converted to a new complex III by heating
with pyridine for approximately 30 min. The reaction was quite fast
in aqueous pyridine and was very slow in dried distilled pyridine.
A large quantity of III was prepared by taking II and allowing it to
stand in aqueous pyridine for several days after heating. A quantity of
acetone was added and the solution was concentrated by flash evaporation.
Fine violet crystals precipitated from the solution. These were filtered
off, washed with water and acetone, and dried. This proved to be the
dihydroxy phosphorous (V) complex, TPP P(V) (OH)$_2^+$Cl$^-$. Calcd.
C$_{44}$H$_{30}$N$_4$O$_2$PCl $\cdot$ 5H$_2$O C, 65.80; H, 5,02; N, 6.97; P, 3.86, Cl, 4.41:
Found: C, 65.52; H, 4.27; N, 6.90; P, 4.29; Cl, 5.55.[3]
λ_{max} (MeOH) 424$_{nm}$ (250,000), 515 sh, 555 (14,000), 593 (3,200).
IR(KBr) 1070cm^{-1}, 1032, 1010, 900, 790, 752, 700, 685.
Pmr(CDCl$_3$) 7.77ppm (m,m,p-H), 8.0 (m, o-H), 8.92 (d, β-H).

Results and Discussion:

Physical characterization: Both II and III could be precipitated
from methanol solutions by the addition of aqueous sodium perchlorate.
This strongly indicated that both could be formulated as cationic complexes.
This was supported by the solution molecular weight data which suggested that

II ionized in ethanol giving an apparent molecular weight approximately
one half of the theoretical value.

The electronic spectra (Fig.1) of both II and III are consistent with
a phosphorus (V) species in the plane of the porphyrin macrocycle.[2]

Calculations by Gouterman *et al.* have shown that phosphorus (III) species are expected to be out of the porphyrin plane and to possess a "hyper"[4] spectra. The phosphorus (V) species are apparently in plane and have a "normal" metalloporphyrin spectra. However, in the TPP complexes substitution of a chlorine for a hydroxyl ligand results in a 10 nm shift in the position of the Soret band. This is significantly more than the 4 nm shift observed by Gouterman in the presumed replacemnt of both hydroxyl ligands by fluoride ion.[2] This may be a result of the change from formally D4h symmetry to C4v symmetry in going from III to II.

The infrared spectra of both II and III are consistent with a phosphorus bound to a TPP macrocycle. The bands between 895-900 cm^{-1} are assigned as P-O stretching vibrations, based on analogy with other phosphorus complexes.[5] The intensity of this band in III is approximately twice that in II as expected. In addition a shift in the three bands at 980 cm^{-1}, 976 cm^{-1}, and 962 cm^{-1} in TPP to 1070 cm^{-1}, 1032 cm^{-1}, and 1010 cm^{-1} in both II and III is consistent with "metal" insertion into the porphyrin ring.[6] Broad weak OH bands are also observed at about 3400 cm^{-1}.

NMR: The nmr spectra of II and III are most unexpected and deserve special comment. In CDCl3 II shows an unsymmetrical doublet-of-doublets for the β-pyrrole hydrogens at 8.90 ppm and 9.16 ppm in a ratio of 2:6. The peak centered at 9.16 ppm is split by 4.2 Hz and that at 8.9 ppm by 3.0 Hz. This splitting is apparently the $^{31}P-^{1}H$ coupling. Such coupling with the relatively remote β hydrogens is not unusual and indeed is expected. A variety of metalloporphyrins have been shown to have extensive coupling between a metal center and the β-hydrogens.

Freshly prepared III in CDCl$_3$ shows only one doublet in the β-H

region of the nmr. It is centered at 8.92 ppm with $J(^{31}p-H)$, 3.0 Hz.

However, if III is allowed to stand in $CDCl_3$ for any period of time a

new doublet centered at 9.16 ppm, $J(^{31}P-^1H)$ 4.2 Hz, appears and gradually

grows in intensity (Fig. 2). If this proceeds long enough, II is generated.

Thus it appears that $^-$III either has the remarkable ability (shared with

several other metalloporphyrins)[9] to abstract a Cl^- from the solvent

or is undergoing intra- or inter- molecular ligand exchange. Compound III

is stable indefinitely in d^6-DMSO and shows only a single doublet $J(^{31}P-^1H)$

= 3.0 Hz, at 8.9 ppm.

In addition, while III shows the expected two multiplets for the O-H

and the m, p-H (ratio 2:3) of the meso phenyl rings, II gives an unexpected

triplet. The peaks at 7.58 ppm, 7.75 ppm, and 7.92 ppm are assigned as

the para, meta, and ortho hydrogens respectively (ratios 1:2:2). These

peaks appear as a single broad peak, unresolved on the T-60 but clearly

resolved on the 100M Hz instrument. In a coordinating solvent such as DMSO,

the two multiplets of the phenyl hydrogens in III collapse to form one

broad single peak which is unresolvable on the T-60.

The nonequivalence of the β-hydrogens indicates that, in solution

at least, the phosphorus may be asymmetrically coordinated to the

porphyrin ring or may have an out-of-plane structure.[10] This is further

supported by the non-equivalence of the meta and para meso phenyl hydrogens.

The fact that a change of solvent from non-coordinating $CDCl_3$ to coordinating

DMSO changes the spectra indicates that the solvent plays a strong role in

the solution structure of both II and III. This may be due to dimerization

of II and III in chloroform solutions which can be reversed upon coordination

by DMSO. The analysis of this phenomena is complicated by the apparent

reaction of III in chlorinated

solvents. Further work in this area may help elucidate the structures of II and III in solution.

Chemistry

The same synthetic method that produced II and III also resulted in some unidentified products. III is prepared from II by reaction with water in pyridine as in equation 1.

$$\text{TPP P(V)OHCl}^{+} + \text{H}_2\text{O} \xrightarrow{\text{pyridine}} \text{TPP P(V)(OH)}_2^{+} + \text{HCl}$$
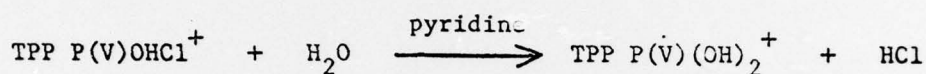
The pyridine scavenges the HCl produced and drives the reaction forward.

If water instead of methanol is used to hydrolyze the initial reaction mixture the only isolatable product appears to be I although it has proven to be very difficult to purify.

I appears to be identical with III based on visible spectra and ir. Another product which appears identical to II in the visible spectra can also be isolated under some conditions. It has no band at 900cm^{-1} in the ir and has a Cl/N indicative of 3-4 chlorines per mole of porphyrin. Its identity is unknown but may be the dichloro derivative of III.

Both II and III proved to be extremely stable towards demetallation. Whereas the OEP complexes were dematallated by CH$_2$Cl$_2$/HCl the TPP complexes proved to be resistant. Indeed these compounds were not demetaliated by 100% trifluoroacetic acid even after several hours. Both complexes appeared to be stable to the action of oxidizing agents such as H$_2$O$_2$ (although gradual ring oxidation seems to occur), but not

to reducing agents. The two complexes could be demetallated without decomposition by reduction with aqueous hydrazine. Treatment of II or III with 64% aqueous NH_2NH_2 results in changes which are visible in the electronic spectra. The complexes appear to pass through several intermediates and within 48 hours are quantitatively demetallated forming free TPP and an unidentified phosphorus species. Presumably the phosphorus is reduced from $P^V \rightarrow P^{III} \rightarrow$? Thallium (III) porphyrins also show this susceptibility to reductive demetallation.[8]

It might be useful here to point out the rather substantial differences between the P(V) OEP complexes and those of TPP reported here.

1. Although all the complexes appear to be cationic, the TPP species are completely insoluble in water.

2. The replacement of a hydroxyl ligand by a chloride ligand in the TPP species results in a much greater shift to the red than in the analogous OEP complexes.

3. While the OEP chelate shows the expected nmr pattern the various TPP analogs show abnormal spectra with non-equivalence of the β-hydrogens.

4. No $^{31}P-^1H$ coupling is observed in the OEP derivatives.

5. Finally, the TPP compounds are much more stable towards demetallation than the OEP complexes. This is represented by the fact that while the OEP chelate is demetallated rapidly by CH_2Cl_2/HCl the TPP compound is stable toward 100% trifluoroacetic acid (TFA) for several hours. The use of the stability index (S_i) predicts that P(V) should be an extremely stable species in a porphyrin complex.[4] Using values of r_i (ionic radii) = 34 pm and EN (Pauling electronegativity) = 2.1 we find a

stability index of 30.88. Buchler has found reasonable agreement between this quantity and stability orders. Other group VA metals have stability indexes of 21.8 and 16.8 for As and Sb respectively. As porphyrin complexes, both of these have been found to belong to stability order I as described by Faulk.[11] Since the S_i for P(V) is even larger it not unexpectedly also falls into this class for the TPP complex. It is quite interesting to find that the OEP complex belongs to class III in variance with its calculated S_i. This may be due to an intrinsic thermal lability as the tervalent As, Sb and Bi OEP complexes are decomposed by heating to 60°C in solvent.[8] There is no information available for the corresponding TPP compounds. It is difficult to assign a reason for the discrepancy between the TPP and OEP P (V) complexes but it may be related to the steric bulk of the meso phenyl rings, or the reduced basicity of the central nitrogen atoms relative to OEP.

Structure: An unambiguous structure for the P(V) porphyrin complexes has not yet been reported. The calculations of Gouterman et al. indicate an in plane structure with axial ligands.[2] However, the unusual nmr spectra may be due to either a dimerization reaction of solvent effects on the conformation of the phenyl rings in solution.

We have succeeded in growing crystals of III from aqueous solvents but such crystals do not diffact x-rays sufficiently for a crystal structure. However, we have grown crystals from non-aqueous solvents, and hopefully these will soon permit a crystal structure determination.

Acknowledgments:

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Figure Captions:

Figure 1. Absorption spectrum of III (dihydroxy)(tetraphenylporphinato)-
phosphorus (V) chloride in methanol.

Figure 2. T-60 nuclear magnetic resonance spectra of various phosphorus
tetraphenylporphine chelates in $CDCl_3$. (a) Freshly prepared
III (ratio of 8.9 ppm β-hydrogen peak to that of 9.16
is 8:0). (b) III after several hours (ratio 6:2).
(c) III after 24 hours (ratio 4:4). (d) II (ratio 2:6).
The peak at about 7.2 ppm is residual $CHCl_3$ from the
deuterated solvent. Note also the collapse of the ortho
and meta-para meso phenyl hydrogen peaks from two
peaks in (a) to one broad peak in (d). The broad peak in
(d) is resolvable on a 100 Mhz instrument and appears as a
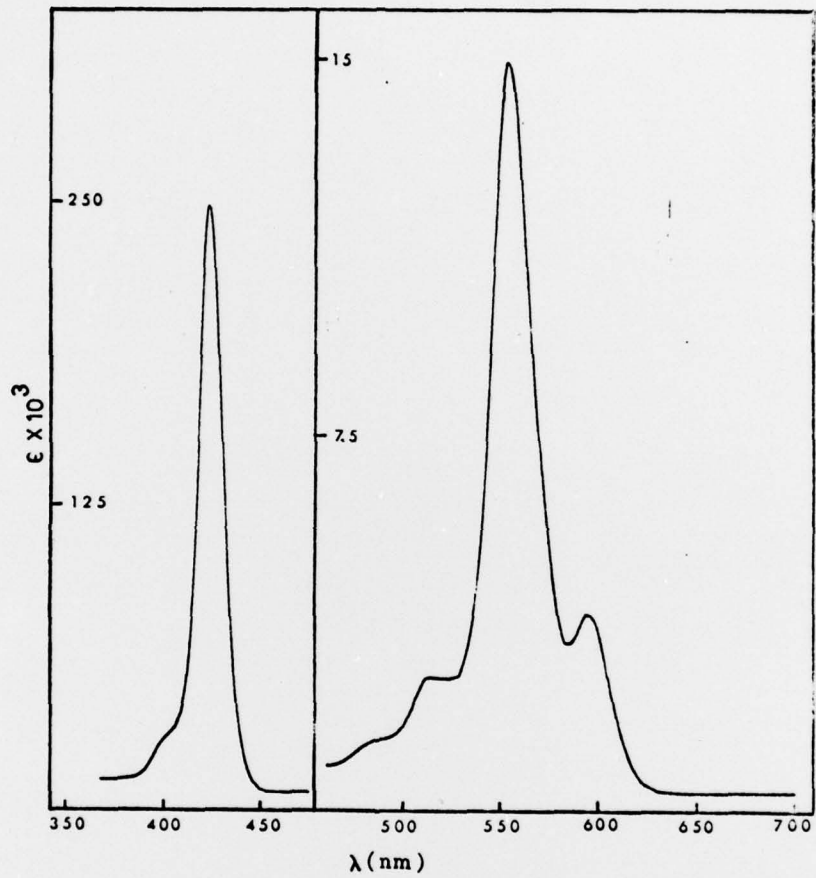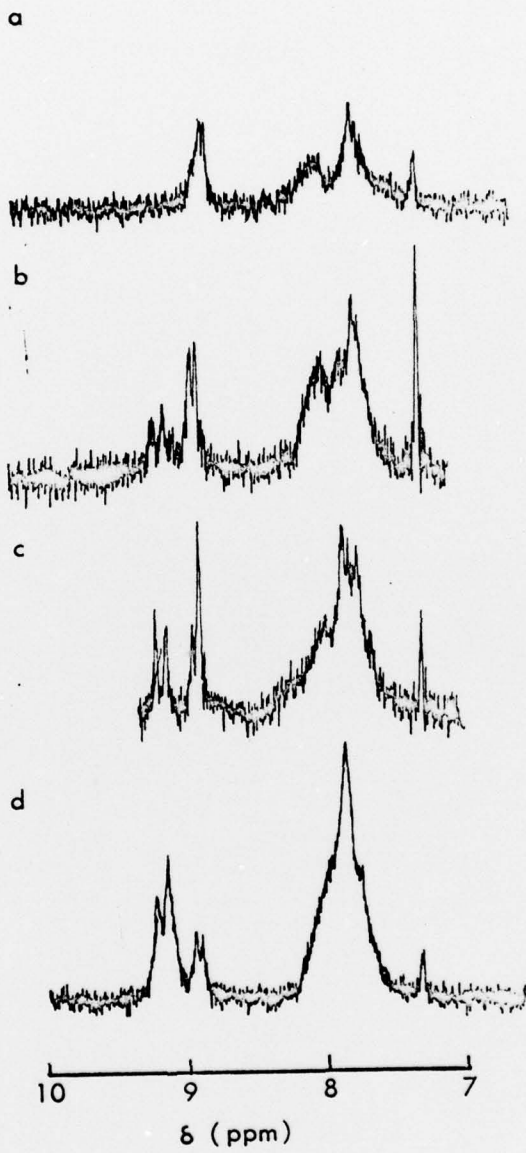triplet (see text).

Fig. I.

a

b

c

d

10   9   8   7
δ (ppm)

Fig. 2.