taken from Cromer.[39] The computer programs used are listed elsewhere.[36]

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Registry No. $[CuClP(t\text{-}Bu)_3]_4$, 83731-72-0; $[CuBrP(t\text{-}Bu)_3]_4$, 83731-73-1; $[CuIP(t\text{-}Bu)_3]_4$, 83731-74-2; $[Cu(P(t\text{-}Bu)_3)_2]Cl$, 83731-75-3; $[Cu(P(t\text{-}Bu)_3)_2]Br$, 83731-76-4; $[Cu(P(t\text{-}Bu)_3)_2]I$, 83731-77-5.

Supplementary Material Available: Listings of torsion angles in the coordinated $P(t\text{-}Bu)_3$ ligand (Table V), typical values for the distances and angles in coordinated $P(t\text{-}Bu)_3$ (Table VI), anisotropic temperature factors (Table VIII), interatomic distances and bond angles in the phosphine (Table IX), the average geometry of coordinated $P(t\text{-}Bu)_3$ (Table X), and observed and calculated structure factors (Table XI) (27 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Dihydroxo(5,10,15,20-tetraphenylporphinato)phosphorus(V) Hydroxide Dihydrate[1]

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The structure of dihydroxo(5,10,15,20-tetraphenylporphinato)phosphorus(V) hydroxide dihydrate, $(C_{44}H_{30}O_2P^+)(OH^-)\cdot 2H_2O$, has been determined from three-dimensional diffractometer data. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.636$ (4) Å, $b = 13.953$ (3) Å, $c = 17.592$ (4) Å, $\beta = 90.21$ (2)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by full-matrix least-squares methods to yield a final R factor of 0.090. This is the first reported structural analysis of a "metalloporphyrin" where the central ion is a nonmetal. The coordination geometry is distorted octahedral with the phosphorus atom displaced 0.09 Å from the mean plane of the pyrrole nitrogen atoms. The P–N bond lengths range from 1.87 (1) to 1.92 (1) Å. The two P–O distances are 1.644 (8) and 1.545 (8) Å. The porphyrin ring shows marked S_4 deviations from planarity. There is extensive hydrogen bonding between the axial hydroxyl groups, the hydroxide counterion and the waters of hydration forming quasi-linear hydrogen-bonded polymers.

Introduction

Porphyrin complexes of almost all the metallic elements are known.[3] Complexes with the metalloids arsenic and silicon have also been reported.[4] Complexes with a nonmetal, phosphorus, have also been characterized by using the synthetic macrocycles octaethylporphyrin (OEP)[5] and *meso*-tetraphenylporphyrin (TPP).[6] For the OEP complexes, evidence has been presented for phosphorus in both the III and V oxidation states. Surprisingly, several differences have been noted between analogous complexes with the two porphyrins. The phosphorus(V) ion was postulated to lie in the plane of the macrocycle in the OEP complex, but in some of the TPP complexes, NMR data suggested the central atom was out of the plane. The complexes of the two porphyrins also show a surprising difference in stability. While the TPP complex falls into the highest stability class (i.e., the metal is not removed by strong acid), the OEP complex is decidedly less stable, the phosphorus ion being removed by traces of HCl in CH_2Cl_2. However, the OEP complex is stable in alcoholic solvents.

The structure of phosphorus(V) porphyrins would also be of interest to show the effects of small ions like phosphorus(V) on the planarity of the macrocycle. Hoard has calculated that, if the radius of the central "hole" is less than 1.96 Å, the macrocycle must undergo buckling so that there are S_4 deviations from planarity.[7] This was borne out by the two crystalline forms of nickel(II) octaethylporphyrin.[8,9] Phos-

Table I. Crystal Data for $(C_{44}H_{30}O_2P^+)(OH^-)\cdot 2H_2O$[a]

space group: $P2_1/c$
$a = 14.636$ (4) Å
$b = 13.963$ (3) Å
$c = 17.592$ (4) Å
$\beta = 90.21$ (2)°
$V = 3595$ (3) Å^3
mol wt = 730.8

$Z = 4$
d(calcd) = 1.35 g cm^{-3}
d(measd) = 1.32 g cm^{-3}
$\mu = 11.2$ cm^{-1} (Cu Kα radiation)
$F(000) = 1528$

systemic absences	$h0l$, l odd; $0k0$, k odd
space group	$P2_1/c$
ω-scan rate	2–20° min^{-1}
scan range	$(0.6 + 0.14 \tan \omega)$°
max $(\sin \theta)/\lambda$	0.50° (100° in 2θ)
total unique reflcns	3623
NO (reflcns with $I > 2.5\sigma_I$)	1190
NV (no. of variables)	217
max shift/error on last cycle	0.09
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.090
$R_w = (\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2)^{1/2}$	0.092
SEF = $(\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(\mathrm{NO} - \mathrm{NV}))^{1/2}$	1.77

[a] In this and subsequent tables, the estimated standard deviation of the least significant figure is shown in parentheses.

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(2) (a) Department of Biochemistry and Biophysics, Texas A&M University. (b) Connecticut College. (c) Deceased; formerly of the Department of Chemistry, Texas A&M University. (d) University of Vermont.

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phosphorus(V) might be expected to have an even smaller M–N distance than found in the tetragonal form of NiOEP, which has the smallest reported radius of the macrocyclic "hole" of any complex with a fully conjugated porphyrin.

For these reasons, when we were able to grow suitable crystals of dihydroxo(tetraphenylporphinato)phosphorus(V) hydroxide dihydrate, we felt that an X-ray crystallographic structure determination of this complex would be of interest.

Experimental Section

Reddish purple crystals of $((OH)_2(TPP)P^+)(OH^-)\cdot 2H_2O$ were obtained from a methanol solution after standing several months. The starting material was $((OH)_2(TPP)P^+)(Cl^-)\cdot 5H_2O$,[6] but it was the hydroxide salt that eventually crystallized. There was no evidence for chloride ions in the crystal structure. Even after this long period of crystallization, the crystals obtained were rather small. The crystal chosen for intensity measurements was one of the larger ones. It was a rod-shaped crystal measuring 0.028 × 0.055 × 0.202 mm. It was mounted in a capillary at an arbitrary orientation.[10]

Crystal data are listed in Table I. An Enraf-Nonius CAD-4 computer-controlled diffractometer at the Molecular Structure Corp., College Station, TX, was used both for the determination of the lattice parameters and for the subsequent intensity data collection. The radiation (Cu $K\alpha$, $\lambda = 1.54184$ Å) was monochromatized by pyrolitic graphite. The cell parameters were obtained by least-squares refinement of the setting angles for 24 reflections. The density was determined by the flotation method using an aqueous zinc nitrate solution. The systematic absence uniquely determined the space group $P2_1/c$ (C_{2h}^5, No. 14).

The diffracted intensities were collected by using the ω–2θ scan technique. A group of three standard reflections was measured periodically. The random variation of their intensities was no more than ±3%, and no corrections were made. Likewise, no absorption corrections were made. The small size of the crystal and low absorption coefficient seemed to justify the neglect of absorption effects. Transmission factors were estimated to be between 0.80 and 0.97, with most being closer to the higher value.

The standard deviation of the intensity was calculated in terms of counting statistics alone as $I = S(C - RB)$ and $\sigma(I) = [S^2(C + R^2B) + (pI)^2]$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time (2.0 in this case), B is the total background count, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.04. Structure factors were calculated in the usual way by assuming ideally imperfect monochromatization.

Determination and Refinement of the Structure

The position of the phosphorus atom was determined from a Patterson synthesis. Additional Fourier maps showed all the atoms of the porphyrin ring together with the two oxygen atoms bonded axially to the phosphorus atom and the oxygen atom belonging to the hydroxide counterion. Two other peaks were also found, which were attributed to the presence of two waters of crystallization.

In least-squares calculations, the function minimized was $\sum w(F_o - F_c)^2$. In the initial stages of refinement unit weights were applied, but in the final cycles, a statistical weighting scheme, $w = 1/\sigma_{F^2}$, was used. Because of the limited amount of data, it was felt that anisotropic refinement was not justified so isotropic thermal motion was assumed. Difference syntheses showed only five peaks corresponding to hydrogen atom positions on the porphyrin ring. In addition, six peaks were located near the oxygen atoms, one each for O(1), O(2), O(4), and O(5) and two for O(3). No evidence was found for the seventh hydrogen atom expected to be on O(4) or O(5). As a result, it is not clear which of these is the hydroxide ion and which is the second water molecule.

Calculated hydrogen atom positions (C–H = 1.00 Å) were used in the structure factor calculations for the atoms on the porphyrin macrocycle and phenyl rings. The observed hydrogen atom positions around the oxygen atoms were also inserted into the structure factor calculations. An isotropic temperature factor of 4.0 Å^2 was assumed for all hydrogen atoms. No hydrogen atom parameters were refined.

A structure factor calculation with all reflections gave an R value of 0.15. A final difference Fourier synthesis showed a maximum electron density of 0.34 e Å^{-3}. No physical significance was attributed to this or any other peak in the final difference map. There was still no evidence for the seventh hydrogen atom bonded to the oxygen atoms. On a typical Fourier map the peak height of a carbon atom was 2.0–2.7 e A^{-3}, while for a hydrogen atom it was 0.3–0.6 e A^{-3}.

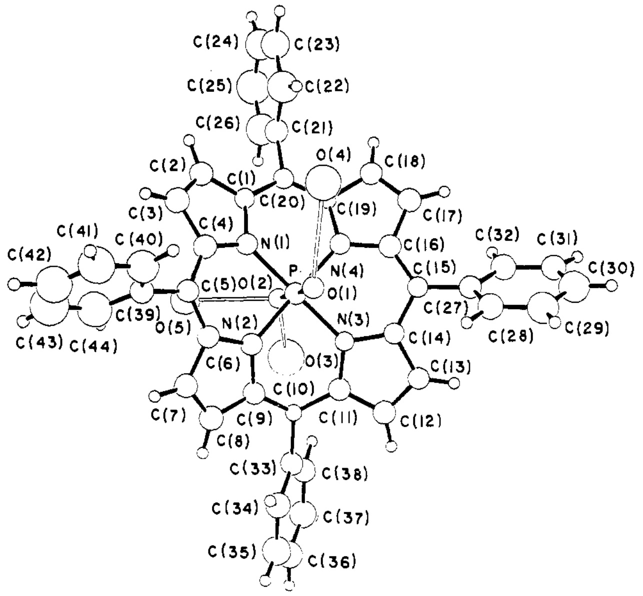

Figure 1. ORTEP[16] drawing of the structure of dihydroxo(tetraphenylporphinato)phosphorus(V) hydroxide dihydrate. The thermal ellipsoids for non-hydrogen atoms are drawn for 30% probability. Those for hydrogen atoms are drawn to scale. Hydrogen atoms are numbered the same as the carbon atom to which they are attached. Hydrogen atoms attached to oxygens are not shown. Hydrogen bonds to O(1) and O(2) are drawn as open bonds.

No evidence of secondary extinction was found. Corrections for anomalous dispersion were applied to all non-hydrogen atoms.[11] Scattering factors were from ref 12. Neutral atoms were assumed.

Final positional parameters are given in Table II. Most of the calculations were performed on a PDP 11/40 computer with use of the Enraf-Nonius structure determination package (SDP).[13] Some calculations were also performed on an Amdahl 470V/6 computer by using programs among those previously listed.[14] Use was also made of the PDP 11/40 Vector General Graphics System.[15]

Results and Discussion

The structure of the porphyrin cation is shown in an ORTEP[16] drawing in Figure 1. A stereoview is shown in Figure 2. The phosphorus atom, which is formally in the V oxidation state, is octahedrally coordinated. Two hydroxide ions are bonded axially to complete the coordination. The phosphorus atom does not lie in the plane of the porphyrin but is displaced 0.09 Å (ca. 20 times the estimated standard deviation) toward O(2) from the mean plane of the pyrrole nitrogen atoms. The P–O bond lengths are therefore nonequivalent. The P–O(2) distance is 1.545 (8) Å, while the P–O(1) distance is 1.644 (8) Å. It is clear that the porphyrin macrocycle blocks a closer approach of O(1). The mean nonbonded contact between O(1)

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Table II. Fractional Coordinates and Isotropic Thermal Motion Parameters Derived from the Least-Squares Refinement[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
P	−0.2503 (3)	0.1132 (4)	0.0207 (3)	2.9 (1)	C(21)	−0.016 (1)	0.333 (1)	0.0995 (9)	3.5 (4)
O(1)	−0.2952 (7)	0.0756 (7)	0.1008 (5)	2.8 (3)	C(22)	0.007 (1)	0.358 (1)	0.1719 (11)	6.2 (6)
O(2)	−0.2103 (7)	0.1512 (7)	−0.0547 (5)	2.5 (2)	C(23)	0.076 (1)	0.424 (1)	0.1841 (10)	5.2 (5)
O(3)	−0.2779 (8)	0.3123 (9)	−0.1171 (6)	5.7 (3)	C(24)	0.121 (1)	0.468 (1)	0.1282 (10)	6.0 (6)
O(4)	−0.2137 (9)	0.1543 (9)	0.2363 (7)	7.1 (4)	C(25)	0.098 (1)	0.446 (2)	0.0562 (11)	7.8 (7)
O(5)	−0.1819 (10)	0.0948 (11)	−0.2016 (8)	9.2 (4)	C(26)	0.031 (1)	0.378 (1)	0.0414 (10)	6.2 (6)
N(1)	−0.2548 (8)	0.2382 (9)	0.0621 (7)	2.8 (3)	C(27)	−0.102 (1)	−0.168 (1)	0.1107 (9)	3.1 (4)
N(2)	−0.3735 (8)	0.1258 (9)	−0.0151 (6)	2.9 (3)	C(28)	−0.159 (1)	−0.224 (1)	0.1518 (9)	3.9 (5)
N(3)	−0.2512 (8)	−0.0142 (9)	−0.0121 (6)	2.3 (3)	C(29)	−0.132 (1)	−0.309 (1)	0.1869 (10)	5.5 (5)
N(4)	−0.1343 (8)	0.0953 (9)	0.0651 (6)	2.7 (3)	C(30)	−0.039 (1)	−0.336 (1)	0.1805 (10)	5.7 (5)
C(1)	−0.180 (1)	0.297 (1)	0.0776 (8)	2.5 (4)	C(31)	0.021 (1)	−0.282 (1)	0.1410 (9)	3.7 (4)
C(2)	−0.212 (1)	0.387 (1)	0.1032 (8)	3.4 (4)	C(32)	−0.008 (1)	−0.197 (1)	0.1060 (9)	4.0 (5)
C(3)	−0.303 (1)	0.384 (1)	0.1089 (9)	3.7 (4)	C(33)	−0.409 (1)	−0.050 (1)	−0.1779 (9)	3.2 (4)
C(4)	−0.330 (1)	0.292 (1)	0.0788 (8)	3.3 (4)	C(34)	−0.503 (1)	−0.075 (1)	−0.1813 (9)	3.8 (5)
C(5)	−0.420 (1)	0.267 (1)	0.0601 (8)	3.0 (4)	C(35)	−0.535 (1)	−0.117 (1)	−0.2487 (10)	5.1 (5)
C(6)	−0.437 (1)	0.194 (1)	0.0113 (8)	2.9 (4)	C(36)	−0.480 (1)	−0.135 (1)	−0.3086 (9)	4.7 (5)
C(7)	−0.518 (1)	0.177 (1)	−0.0328 (8)	3.2 (4)	C(37)	−0.387 (1)	−0.110 (1)	−0.3050 (9)	4.7 (5)
C(8)	−0.500 (1)	0.113 (1)	−0.0869 (9)	3.5 (4)	C(38)	−0.353 (1)	−0.067 (1)	−0.2407 (9)	3.7 (4)
C(9)	−0.411 (1)	0.075 (1)	−0.0752 (8)	3.0 (4)	C(39)	−0.499 (1)	0.326 (1)	0.0850 (9)	3.2 (4)
C(10)	−0.370 (1)	−0.003 (1)	−0.1069 (8)	1.7 (4)	C(40)	−0.521 (1)	0.330 (1)	0.1607 (10)	5.5 (5)
C(11)	−0.296 (1)	−0.054 (1)	−0.0727 (8)	3.1 (4)	C(41)	−0.596 (1)	0.386 (2)	0.1862 (11)	6.9 (6)
C(12)	−0.279 (1)	−0.152 (1)	−0.0792 (9)	3.3 (4)	C(42)	−0.638 (1)	0.437 (2)	0.1381 (11)	6.9 (6)
C(13)	−0.222 (1)	−0.174 (1)	−0.0205 (8)	2.9 (4)	C(43)	−0.619 (1)	0.444 (2)	0.0655 (12)	8.2 (7)
C(14)	−0.204 (1)	−0.088 (1)	0.0214 (8)	2.6 (4)	C(44)	−0.546 (1)	0.387 (1)	0.0358 (11)	6.7 (6)
C(15)	−0.133 (1)	−0.080 (1)	0.0753 (8)	2.6 (4)	H(O1)	−0.283	0.062	0.168	4
C(16)	−0.098 (1)	0.009 (1)	0.0890 (8)	3.2 (4)	H(O2)	−0.232	0.105	−0.078	4
C(17)	−0.008 (1)	0.029 (1)	0.1207 (9)	3.6 (4)	H(O3)	−0.232	0.230	−0.094	4
C(18)	0.009 (1)	0.126 (1)	0.1117 (9)	3.2 (4)	H(O31)	−0.250	0.356	−0.129	4
C(19)	−0.073 (1)	0.167 (1)	0.0800 (8)	1.8 (4)	H(O4)	−0.266	0.207	0.219	4
C(20)	−0.089 (1)	0.263 (1)	0.0812 (8)	2.7 (4)	H(O5)	−0.232	0.105	−0.230	4

[a] Isotropic temperature factors are defined by $T = \exp[-B(\sin^2 \theta)/\lambda]^2$. Parameters for hydrogen atoms bonded to oxygen are given. These were not refined. Positions for the remaining hydrogen atoms, which were calculated, are given in the supplementary material.

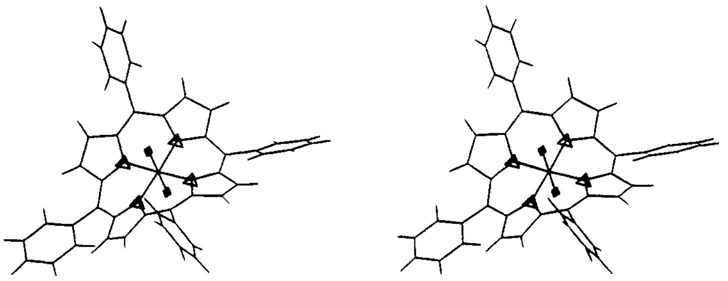

Figure 2. Stereoview of a single molecule. Nitrogen atoms are marked by tetrahedra, and oxygen atoms by octahedra.

and the pyrrole nitrogen atoms is 2.44 (1) Å as compared to 2.51 (2) Å for O(2).

As expected, the bond lengths between the phosphorus atom and the pyrrole nitrogen atoms are short compared to those normally found in metalloporphyrins. The P–N distances, which range from 1.870 (10) to 1.916 (11) Å (average of 1.890 (15) Å), are the shortest M–N distances yet reported for a complex with a fully conjugated porphyrin. The average N–N cross-ring distance is 3.78 (2) Å, corresponding to an average radius of 1.89 Å. The P–N bond lengths agree well with the value predicted by Sayre, Gouterman, and Connell.[5] The constraints of the macrocycle cause the P–N bonds to be considerably longer than is normally found. P–N bond lengths generally range from 1.60 to 1.65 Å.[17]

Table VII. Least-Squares Planes

(A) Angles (deg) between Least-Squares Planes

	plane 2	plane 3	plane 4	plane 5
plane 1	24.8	24.9	29.4	27.3
plane 2		34.4	54.2	38.3
plane 3			39.2	52.1
plane 4				35.8

(B) Equations of Planes[a]

plane 1: [N(1)–N(4)]
$-5.672x - 4.550y + 15.195z = 1.311$

plane 2 (pyrrole ring 1): [N(1), C(1)–C(4)]
$0.522x - 4.930y + 16.444z = -0.293$

plane 3 (pyrrole ring 2): [N(2), C(6)–C(9)]
$5.033x + 9.645y - 11.213z = -0.485$

plane 4 (pyrrole ring 3): [N(3), C(11)–C(14)]
$17.558x + 2.696y - 10.295z = -2.817$

plane 5 (pyrrole ring 4): [N(4), C(16)–C(19)]
$-5.728x + 1.999y + 16.017z = 2.012$

[a] All planes are unweighted. x, y, z are in monoclinic fractional coordinates. Deviations from these planes and data involving planes of the phenyl groups are given in supplementary material.

Although the four pyrrole nitrogen atoms are coplanar, the macrocycle is markedly nonplanar. Angles between least-squares planes of interest are given in Table VII. Hoard[7] has predicted that an S_4 deviation from planarity such as observed here would be the optimum method of relieving strain when the macrocyclic "hole" contracts to accommodate a small central atom. The interplanar angles between adjacent pyrrole rings range from 34.3 to 39.2°. This compares with an in-

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(17) Brown, I. D.; Brown, M. C.; Hawthorne, F. C. "BIDICS: Bond Index to the Determinations of Inorganic Crystal Structures"; McMaster University: Hamilton, Ontario, Canada, 1978. Earlier volumes of this series also contain similar P–O bond lengths.

Table VIIIA. Bond Lengths (Å) and Angles (deg)[a]

P-O(1)	1.644 (8)	N(3)-C(14)	1.374 (14)	C(8)-C(9)	1.431 (16)	C(18)-C(19)	1.450 (16)
P-O(2)	1.545 (8)	N(4)-C(16)	1.379 (14)	C(9)-C(10)	1.370 (15)	C(19)-C(20)	1.356 (15)
P-N(1)	1.892 (1)	N(4)-C(19)	1.368 (13)	C(10)-C(11)	1.421 (15)	N(1)-N(2)	2.703 (15)
P-N(2)	1.916 (11)	C(1)-C(2)	1.415 (16)	C(11)-C(12)	1.394 (15)	N(1)-N(3)	3.758 (16)
P-N(3)	1.870 (10)	C(1)-C(20)	1.411 (15)	C(12)-C(13)	1.363 (15)	N(1)-N(4)	2.663 (16)
P-N(4)	1.884 (10)	C(2)-C(3)	1.344 (16)	C(13)-C(14)	1.434 (15)	N(2)-N(3)	2.652 (15)
N(1)-C(1)	1.398 (14)	C(3)-C(4)	1.442 (17)	C(14)-C(15)	1.412 (14)	N(2)-N(4)	3.794 (15)
N(1)-C(4)	1.364 (14)	C(4)-C(5)	1.411 (16)	C(15)-C(16)	1.365 (16)	N(3)-N(4)	2.662 (15)
N(2)-C(6)	1.408 (15)	C(5)-C(6)	1.356 (15)	C(16)-C(17)	1.459 (16)	C(5)-C(15)	6.426 (19)
N(2)-C(9)	1.380 (13)	C(6)-C(7)	1.430 (15)	C(17)-C(18)	1.385 (16)	C(10)-C(20)	6.445 (18)
N(3)-C(11)	1.367 (14)	C(7)-C(8)	1.334 (15)				

O(1)-P-O(2)	178.3 (5)	C(6)-N(2)-C(9)	110 (1)	C(7)-C(8)-C(9)	109 (1)	C(15)-C(16)-C(17)	125 (1)
O(1)-P-N(1)	87.1 (4)	C(11)-N(3)-C(14)	106 (1)	N(2)-C(9)-C(8)	106 (1)	C(16)-C(17)-C(18)	107 (1)
O(1)-P-N(2)	86.1 (5)	C(16)-N(4)-C(19)	109 (1)	N(2)-C(9)-C(10)	123 (1)	C(17)-C(18)-C(19)	106 (1)
O(1)-P-N(3)	87.6 (5)	N(1)-C(1)-C(2)	109 (1)	C(8)-C(9)-C(10)	130 (1)	N(4)-C(19)-C(18)	109 (1)
O(1)-P-N(4)	88.0 (4)	N(1)-C(1)-C(20)	123 (1)	C(9)-C(10)-C(11)	124 (1)	N(4)-C(19)-C(20)	128 (1)
O(2)-P-N(1)	91.6 (5)	C(2)-C(1)-C(20)	127 (1)	N(3)-C(11)-C(10)	119 (1)	C(18)-C(19)-C(20)	122 (1)
O(2)-P-N(2)	92.7 (5)	C(1)-C(2)-C(3)	110 (1)	N(3)-C(11)-C(12)	112 (1)	C(1)-C(20)-C(19)	119 (1)
O(2)-P-N(3)	93.6 (5)	C(2)-C(3)-C(4)	105 (1)	C(10)-C(11)-C(12)	126 (1)	P-N(1)-C(1)	126 (1)
O(2)-P-N(4)	93.3 (5)	N(1)-C(4)-C(3)	111 (1)	C(11)-C(12)-C(13)	106 (1)	P-N(1)-C(4)	128 (1)
N(1)-P-N(2)	90.5 (5)	N(1)-C(4)-C(5)	125 (1)	C(12)-C(13)-C(14)	108 (1)	P-N(2)-C(6)	125 (1)
N(1)-P-N(3)	174.7 (5)	C(3)-C(4)-C(5)	124 (1)	N(3)-C(14)-C(13)	109 (1)	P-N(2)-C(9)	125 (1)
N(1)-P-N(4)	89.7 (5)	C(4)-C(5)-C(6)	120 (1)	N(3)-C(14)-C(15)	127 (1)	P-N(3)-C(11)	129 (1)
N(2)-P-N(3)	88.9 (5)	N(2)-C(6)-C(5)	127 (1)	C(13)-C(14)-C(15)	123 (1)	P-N(3)-C(14)	125 (1)
N(2)-P-N(4)	174.0 (5)	N(2)-C(6)-C(7)	105 (1)	C(14)-C(15)-C(16)	118 (1)	P-N(4)-C(16)	126 (1)
N(3)-P-N(4)	90.4 (5)	C(5)-C(6)-C(7)	128 (1)	N(4)-C(16)-C(15)	127 (1)	P-N(4)-C(19)	125 (1)
C(1)-N(1)-C(4)	105 (1)	C(6)-C(7)-C(8)	110 (1)	N(4)-C(16)-C(17)	108 (1)		

[a] Only those bond parameters involving the phosphorus coordination sphere and those involving the porphyrin skeleton are included. Those involving the phenyl groups may be found in the supplementary material. Some nonbonded contacts of interest are also given.

terplanar angle of 32.8° in the tetragonal form of nickel octaethylporphyrin.[8] In that case the radius of the macrocyclic "hole" was 1.929 Å.

The observed geometry where the central atom is displaced toward one of the two chemically equivalent ligands is unusual for porphyrin complexes and deserves some comment. It is of interest to note that, in the only other reported group 5A metalloporphyrin where the central ion is in the V state, $((OH)_2(OEP)Sb^+)(ClO_4^-)$,[18] the metal ion is in the plane of the macrocycle. The most closely analogous situation is found in dichloro(tetra-*p*-tolylporphinato)molybdenum(IV),[19] where the two axial Mo–Cl bond lengths are nonequivalent. However, in that case the metal ion is in the plane of the macrocycle. Because the hydrogen atoms bonded to the oxygen atoms were not unambiguously located, the crystallographic evidence does not conclusively prove the ligands are both hydroxyl groups. One alternative formulation, (OH)(TPP)-P=O, can be eliminated from consideration. The P–O(1) distance (1.644 (8) Å) is that normally found for a phosphorus–oxygen single bond.[17] A phosphorus–oxygen double bond generally is about 1.44 Å. We have eliminated other possible formulations such as $(H_2O)(OH)(TPP)P^{2+}$ or $(H_2O)_2(TPP)P^{3+}$ on the basis of other chemical and physical evidence. Conductivity data clearly indicate a 1:1 electrolyte in both the TPP and OEP complexes.[5,6] Recent work on the titration of the OEP complex (which has a chloride counterion) also confirms the dihydroxy formulation.[20]

Three possible explanations can be postulated for the the out-of-plane displacement of the phosphorus atom in the TPP complexes. However, all of them have their inadequacies. The first possibility assumes a square-pyramidal geometry when the first hydroxyl group is added. It may be that phosphorus ion is not sufficiently strongly coordinating to be pulled back into the plane of the macrocycle when the second hydroxyl group is added on the other side of the porphyrin. Such an explanation, however, would not explain the OEP complexes, where the phosphorus atom is apparently in the plane.

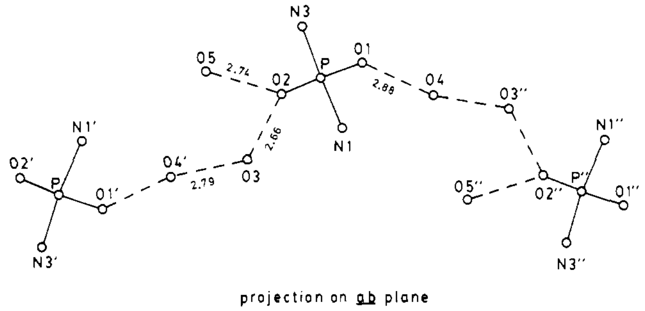

Figure 3. Hydrogen bonding schemes as viewed down the *c* axis. Note the dissimilar environments of O(1) and O(2). Hydrogen-bonded distances are given. The prime superscript refers to the symmetry-related positions generated from the reference molecule by the operation $x' = -0.5 + x$, $y' = 0.5 - y$, $z' = z$. The double prime superscript is related to the primed molecule by a unit translation along *a*.

The second possibility arises from a consideration of the hydrogen bonding. There is a hydrogen-bonding network roughly parallel to the *a* direction. This involves both hydroxyl groups, the hydroxide counterion, and both waters of hydration. (See Figure 3.) There are two strong hydrogen bonds to O(2) and only one to O(1). This hydrogen-bonding scheme is similar to that found in $((OH)_2(OEP)Sb^+)(ClO_4^-)$, which also contains an ethanol of solvation.[18] However, in that compound each hydroxide ion is involved in only one hydrogen bond.

Consideration of the packing in the unit cell (Figure 4) shows that the porphyrin macrocycle is held in place by interactions between bulky phenyl groups. There are no unusually short contacts. The H–H intermolecular contacts for phenyl groups range from 2.7 to 3.2 Å. H–H distances much shorter than these have been reported (e.g., 2.41 Å in (TPP)InCl).[21] There are only four contacts ≥3.5 Å between

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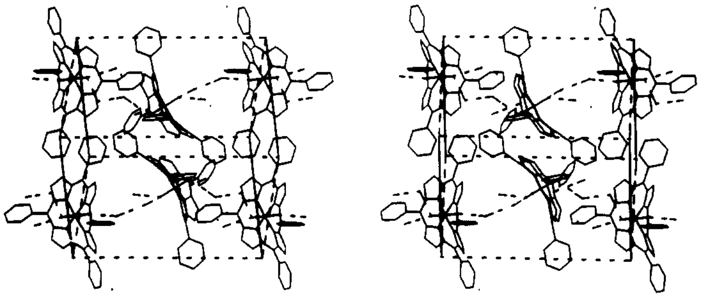

Figure 4. Stereoview of the packing in the unit cell, as viewed approximately down (110). Hydrogen bonds are indicated by dashed lines between atoms. *a*, *b*, and *c* axes are indicated by solid, long dashed, and short dashed lines, respectively. This figure (and Figure 2) was drawn with the aid of computer program PACK.[30]

non-hydrogen atoms other than the hydrogen-bonded distances. However, the porphyrin molecules are allowed little freedom of motion, which would still maintain the optimum packing of the bulky side groups. It may be that the strong hydrogen bonds to O(2) stabilize the arrangement where the phosphorus atom is pulled out of the plane of the relatively rigidly held porphyrin. Such an arrangement would explain the situation in the OEP complexes, since the ethyl groups are less bulky.

The third possibility arises from the observation that TPP complexes are apparently more likely to adopt the type of S_4 ruffling found in this compound. All of the TPP complexes with small metal ions show this type of deviation from planarity.[7b] As previously mentioned, a planar form of nickel octaethylporphyrin has been reported.[9] The H_4TPP^{2+} cation is highly ruffled[22] while the H_4OEP^{2+} and H_3OEP^{+} cations[23-25] are relatively planar. Two forms of the H_2TPP have been reported,[26,27] one ruffled and one planar, whereas only a planar H_2OEP moiety has been reported.[28] It may be possible that the analogous OEP complex of P(V) may adopt a more planar configuration and thus be less able to relieve the strain induced by the small central ion. Since it is not possible for the radius of the planar macrocycle to be less than 1.96 Å,[7] it may be that the phosphorus atom will be accommodated in the plane of the larger central "hole". It would be expected that, if this were the case, the phosphorus ion in planar complexes would be more readily removed than in the ruffled complexes. It is realized that the differences in energies between the ruffled and planar forms are relatively small.[9] The proof of the validity of any of these models obviously depends on future work.

The interplanar angles between the plane of the four pyrrole nitrogen atoms and the planes of the phenyl groups range from 62 to 122°. These values are not unusual for tetraphenylporphyrin compounds.

Both lengths and angles are given in Table VIIIA. As far as the rather limited accuracy of the data will allow comparison, the bond parameters in the macrocycle agree well with those found in other metalloporphyrins. The C_α–C_m–C_α angle, where C_m is the methine carbon atom, is the most sensitive measure of changes in the macrocyclic radius. The average angle in this case is relatively small (120°). This compares to angles of 124.1° in the tetragonal form of nickel octaethylporphyrin[8] and 129.5° in dichloro(octaethylporphinato)tin(IV),[29] in which the macrocycle is planar and has a highly expanded radius.

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Registry No. $((OH)_2(TPP)P^+)(OH^-)\cdot 2H_2O$, 83732-24-5.

Supplementary Material Available: Tables III–VI and VIIIB containing respectively calculated hydrogen atom positions, deviations from the least-squares planes for the macrocyclic skeleton, least-squares plane information for the phenyl groups, observed and calculated structure factors, and bond parameters involving the phenyl groups (23 pages). Ordering information is given on any current masthead page.

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