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MOLECULAR AND CRYSTAL STRUCTURE OF DICHLORO(5,10,15,20-TETRAPHENYLPORPHINATO)PHOSPHORUS(V) CHLORIDE DICHLOROMETHANE SOLVATE

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Abstract—The crystal structure of dichloro(5,10,15,20-tetraphenylporphinato)phosphorus(V) chloride dichloromethane solvate has been determined by X-ray diffraction at ambient temperature. A saddle shape of the *meso*-tetraphenylporphinate disc is attributed to marked S_4 deviation from planarity. The mode of the torsion of four phenyl rings around the C—C bonds connecting these rings to the respective *meso* carbon atoms are also of S_4 character. The phosphorus atom lies just in the mean plane of the porphinate nitrogen atoms. The P—N bond distances range from 1.804(3) to 1.821(3) Å, which are shorter than those observed in $[P(OH)_2(tpp)]^+$ (1.870–1.916 Å), while the axial P—Cl bond distances [2.149(1) and 2.153(1) Å] are significantly longer than the distance expected for the normal covalent P—Cl bond (2.10 Å). This phosphorus porphyrin reveals characteristic features peculiar to the structure of metalloporphyrins with the smallest-sized central cations.

Porphyrin complexes of almost all metals and some semimetals have been prepared, and these elements make the so-called "periodic table of metalloporphyrins".[1] Complexes with the metalloids silicon, arsenic and antimony have also been reported.[2] For complexes with non-metallic elements, the studies have been focused on phosphorus porphyrins.[3] P^{III}, As^{III} and Sb^{III} porphyrins are auto-oxidized to P^{V}, As^{V} and Sb^{V} porphyrins. The stability of P^{V} porphyrins is markedly dependent on the peripheral substituents.[3a] For example, the phosphorus atom in the *meso*-tetraphenylporphyrin (tpp) complex is not removed by strong acid, while the phosphorus in the octaethylporphyrin (oep) complex is removed. Recently, conductive one-dimensional donor–acceptor polymers of phosphorus porphyrins were synthesized.[4] In the series of phosphorus porphyrin complexes, the dichloro(5,10,15,20-tetraphenylporphinato)phosphorus(V) chloride ($[PCl_2(tpp)]Cl$) is one of the most important compounds, because $[PCl_2(tpp)]Cl$ offers some other P–tpp complexes with different axial ligands by substitution of the axial chloro ligands.[3] Therefore, the crystal structure of $[PCl_2(tpp)]Cl$ would be useful in further studying the effect of axial ligands on the structures and properties of phosphorus porphyrin complexes.

Mangani and co-workers have reported the crystal structure of dihydroxo(*meso*-tetraphenylporphinato)phosphorus(V) hydroxide dihydrate.[5] They have suggested that the respective hydroxo ligands are subjected to different degrees of hydrogen bonding and the phosphorus atom is considerably above the plane defined by the porphinate

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nitrogen atoms. Since chloride has less tendency toward Cl···H—C hydrogen bonding than the hydroxo toward O—H···OH$_2$, it can be expected that the X-ray crystallographic study of [PCl$_2$(tpp)]Cl should reveal some aspects of the characteristic features of the structure of porphyrin complexes with the smallest-sized central atoms.

EXPERIMENTAL

Sample preparation

The title compound was prepared according to the procedure of Marrese and Carrano.[6] The crystals used for X-ray diffraction were obtained from a CH_2Cl_2–n-C_7H_{16} solution after standing for several weeks. The elementary analysis indicates [PCl$_2$(tpp)]Cl·CH$_2$Cl$_2$. Found: C, 64.3; H, 3.3; N, 6.5; Cl, 21.5. Calc.: C, 64.7; H, 3.6; N, 6.7; Cl, 21.3%.

Structure determination

A purple crystal was mounted on an automated four-circle diffractometer (Rigaku AFC5R) with graphite monochromatized Cu-K_α radiation (λ = 1.5418 Å) from a fine-focus anode of a 12-kW rotating-anode generator. The experimental details and crystal data are summarized in Table 1. The cell constants were estimated from 25 reflections whose 2θ range were from 54.5 to 54.9°. The ω–2θ scan mode with a scan rate of 16° min^{-1} (in ω) was employed. Corrections were made for Lorentz and polarization factors. Empirical corrections for the absorption were made based on azimuthal (ψ) scans of five reflections.[7] The secondary extinction effect (coefficient = 48.2×10^{-7}) was considered at the final stage of the refinement. The structure was solved by direct methods.[8] The coordinates and anisotropic temperature factors for the non-hydrogen atoms were refined by the full-matrix least-squares procedure based on F with weight $w = 1/\sigma^2(F)$. The positions of hydrogen atoms were idealized (C—H 0.95 Å), assigned isotropic thermal parameters B(H) = 1.2B_{eq}(C) and allowed to ride on their parent carbons. All calculations were performed on a VAXstation 3200 computer with TEXSAN program[9] which used the atomic scattering factors taken from the *International Tables for X-ray Crystallography*.[10] Anomalous dispersion effects were included in the F_c calculation. The final atomic parameters, together with observed and calculated structure factors, have been deposited with the Editor, from whom the copies are available on request. The relevant parameters have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Disregarding the orientational disorder of solvate dichloromethane, the structure refinement provided an R value of 0.054. The disorder model for the dichloromethane yielded an R value of 0.043, where the occupancy factors of two chlorine atoms [Cl(4) and Cl(5)] and the other two atoms [Cl(6) and Cl(7)] were 0.606 and 0.394, respectively, and the same factors of the relevant hydrogen atoms were fixed at 1/2. In this model, the C—Cl bond lengths in the solvate molecule (1.68–1.90 Å) are

Table 1. Crystal data, experimental conditions and refinement details of the [PCl$_2$(tpp)]Cl·CH$_2$Cl$_2$ crystal

Empirical formula	$C_{45}H_{30}N_4PCl_5$	Space group $P2_1/n$	Z 4
Crystal system	monoclinic	V	3919.5(8) Å^3
a	10.701(2) Å	D_{obs}	1.4 g cm^{-3}
b	24.843(3) Å	D_{calc}	1.415 g cm^{-3}
c	14.785(1) Å	μ(Cu-K_α)	41.42 cm^{-1}
β	94.251(9)°	$2\theta_{max}$	123.0°
Formula weight	835.00		
Number of reflections measured		6615	
Number of unique reflections		6250 (R_{int} = 0.049)	
Number of observed reflections [$I \geqslant 3\sigma(I)$]		4096	
Number of variables		522	
R; R_w		0.043; 0.047	
S (goodness of fit indicator)		1.74	
Range of Δ/ρ		−0.24 to 0.57 e Å^{-3}	

more widely spread than those of the alternative model (1.69 and 1.74 Å). The geometry parameters in the porphinate part are not different in the two models beyond the margin of error.

The PLUTO drawing of the molecular structure is shown in Fig. 1,[11] together with the atomic numbering scheme. The pertinent bond distances and angles are given in Tables 2 and 3, respectively. As shown in Fig. 2, the *meso*-tetraphenylporphinate disc shows a saddle shape. The phosphorus atom, which is formally five-valent, is accommodated in the central hole of the porphyrin macrocycle and carries two chlorides. The Cl—P—Cl pivot is linear [179.68(6)°] and the chlorides do not have intermolecular contacts shorter than van der Waals contacts. The two P—Cl bonds are equivalent in bond distance [2.152(1) Å], and are longer than both of those in $[PCl_4]^+$ (1.97 Å) and $[PCl_6]^-$ ions (2.04–2.09 Å) in PCl_5 solid[12] and than the sum of the covalent radii (2.08 Å).[13] The intramolecular nonbonded contacts between the axial chlorine atoms and porphinate nitrogen atoms are considerably shorter than van der Waals contact (3.3 Å);[14] the distances from Cl(1) to N(1), N(3), N(2) and N(4) are 2.793(3), 2.794(3), 2.822(3) and 2.838(3) Å, and from Cl(2) to N(1), N(3), N(2) and N(4) are 2.821(3), 2.829(3), 2.803(3) and 2.806(3) Å, respectively. The P—N distances range from 1.804(3) to 1.821(3) Å and are considerably shorter than 1.96 Å, which is a threshold that a radius of the central hole smaller than this leads the porphyrin macrocycle to buckle from planarity.[5,15] These P—N distances are even shorter than those in $[P(OH)_2(tpp)](OH)\cdot 2H_2O$ [1.87(1)–1.92(1) Å].[5] This indicates that the central hole in the present porphinate is smaller than that in the porphinate of the last complex; the average radii of these holes estimated from the N $\cdots$ N cross-ring distances are 1.813(4) and 1.89(2) Å, respectively. However, the P—N bond distances are considerably longer than general P—N bond lengths, ranging from 1.60 to 1.65 Å.[5] Therefore, the present P—N bond dis-

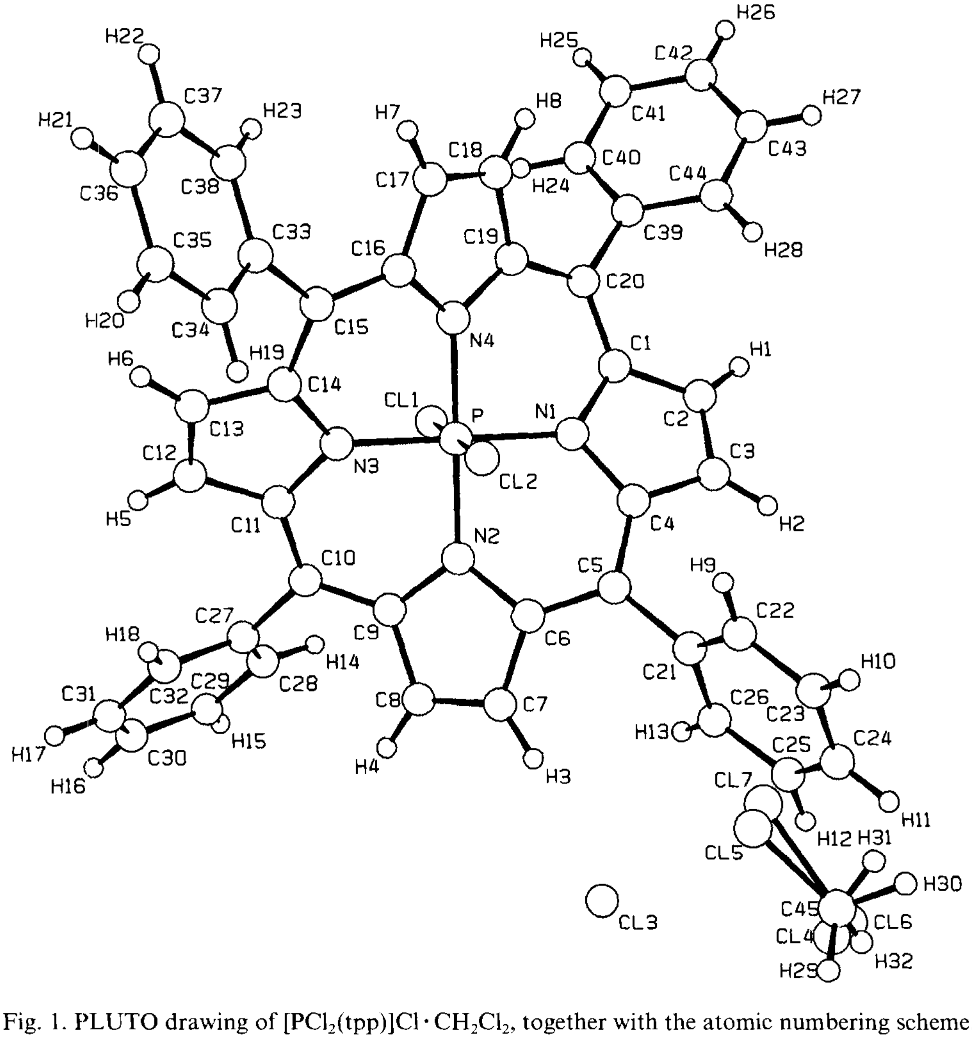

Fig. 1. PLUTO drawing of $[PCl_2(tpp)]Cl\cdot CH_2Cl_2$, together with the atomic numbering scheme.

Table 2. Selected bond distances (Å) with their e.s.d. values given in parentheses

P—Cl(1)	2.153(1)	N(4)—C(19)	1.383(4)	C(12)—C(13)	1.357(5)
P—Cl(2)	2.149(1)	C(1)—C(2)	1.431(5)	C(13)—C(14)	1.407(5)
P—N(1)	1.804(3)	C(1)—C(20)	1.382(5)	C(14)—C(15)	1.301(5)
P—N(2)	1.818(3)	C(2)—C(3)	1.350(5)	C(15)—C(16)	1.385(5)
P—N(3)	1.809(3)	C(3)—C(4)	1.421(5)	C(16)—C(17)	1.420(5)
P—N(4)	1.821(3)	C(4)—C(5)	1.385(5)	C(17)—C(18)	1.361(5)
N(1)—C(1)	1.398(4)	C(5)—C(6)	1.381(5)	C(18)—C(19)	1.429(5)
N(1)—C(4)	1.383(4)	C(6)—C(7)	1.420(5)	C(19)—C(20)	1.393(5)
N(2)—C(6)	1.398(4)	C(7)—C(8)	1.345(5)	C(5)—C(21)	1.489(5)
N(2)—C(9)	1.396(4)	C(8)—C(9)	1.427(5)	C(10)—C(27)	1.495(5)
N(3)—C(11)	1.397(4)	C(9)—C(10)	1.377(5)	C(15)—C(33)	1.484(5)
N(3)—C(14)	1.388(4)	C(10)—C(11)	1.385(4)	C(20)—C(39)	1.488(5)
N(4)—C(16)	1.399(4)	C(11)—C(12)	1.411(5)		

Table 3. Selected bond angles (°) with their e.s.d. values given in parentheses

Cl(1)—P—Cl(2)	179.68(6)	C(12)—C(13)—C(14)	107.5(3)
Cl(1)—P—N(1)	89.3(1)	N(3)—C(14)—C(13)	109.2(3)
Cl(1)—P—N(2)	90.2(1)	C(16)—N(4)—C(19)	107.4(3)
Cl(1)—P—N(3)	89.2(1)	N(4)—C(16)—C(17)	108.2(3)
Cl(1)—P—N(4)	90.8(1)	C(16)—C(17)—C(18)	107.9(3)
Cl(2)—P—N(1)	90.6(1)	C(17)—C(18)—C(19)	108.0(3)
Cl(2)—P—N(2)	89.5(1)	N(4)—C(19)—C(18)	108.2(3)
Cl(2)—P—N(3)	90.8(1)	N(1)—C(1)—C(20)	123.3(3)
Cl(2)—P—N(4)	89.6(1)	C(2)—C(1)—C(20)	127.3(3)
N(1)—P—N(2)	90.3(1)	N(1)—C(4)—C(5)	125.3(3)
N(1)—P—N(3)	178.6(1)	C(3)—C(4)—C(5)	124.7(3)
N(1)—P—N(4)	89.9(1)	C(4)—C(5)—C(6)	118.0(3)
N(2)—P—N(3)	89.7(1)	N(2)—C(6)—C(5)	122.9(3)
N(2)—P—N(4)	179.1(1)	C(5)—C(6)—C(7)	127.3(3)
N(3)—P—N(4)	90.1(1)	N(2)—C(9)—C(10)	124.3(3)
P—N(1)—C(1)	126.4(2)	C(8)—C(9)—C(10)	126.7(3)
P—N(1)—C(4)	126.1(2)	C(9)—C(10)—C(11)	118.9(3)
P—N(2)—C(6)	126.2(2)	N(3)—C(11)—C(10)	122.7(3)
P—N(2)—C(9)	126.8(2)	C(10)—C(11)—C(12)	127.8(3)
P—N(3)—C(11)	127.0(2)	N(3)—C(14)—C(15)	124.6(3)
P—N(3)—C(14)	126.4(2)	C(13)—C(14)—C(15)	125.2(3)
P—N(4)—C(16)	125.5(2)	C(14)—C(15)—C(16)	118.1(3)
P—N(4)—C(19)	126.4(2)	N(4)—C(16)—C(15)	122.9(3)
C(1)—N(1)—C(4)	107.1(3)	C(15)—C(16)—C(17)	127.6(3)
N(1)—C(1)—C(2)	107.8(3)	N(4)—C(19)—C(20)	125.4(3)
C(1)—C(2)—C(3)	107.7(3)	C(18)—C(19)—C(20)	125.0(3)
C(2)—C(3)—C(4)	108.3(3)	C(1)—C(20)—C(19)	117.4(3)
N(1)—C(4)—C(3)	108.5(3)	C(4)—C(5)—C(21)	118.7(3)
C(6)—N(2)—C(9)	106.9(3)	C(6)—C(5)—C(21)	123.0(3)
N(2)—C(6)—C(7)	108.4(3)	C(9)—C(10)—C(27)	119.1(3)
C(6)—C(7)—C(8)	108.0(3)	C(11)—C(10)—C(27)	121.4(3)
C(7)—C(8)—C(9)	108.7(3)	C(14)—C(15)—C(33)	117.7(3)
N(2)—C(9)—C(8)	107.8(3)	C(16)—C(15)—C(33)	123.9(3)
C(11)—N(3)—C(14)	106.4(3)	C(19)—C(20)—C(39)	117.5(3)
N(3)—C(11)—C(12)	108.1(3)	C(1)—C(20)—C(39)	124.4(3)
C(11)—C(12)—C(13)	108.5(3)		

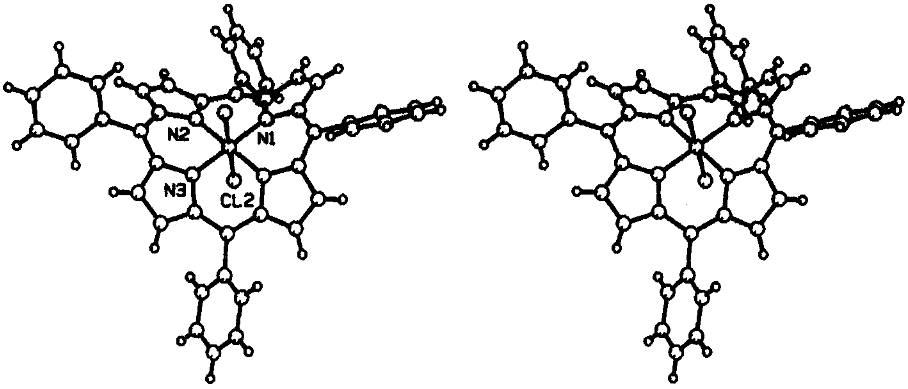

Fig. 2. Stereoview of the $[\mathrm{PCl_2(tpp)}]^+$ chromophore.

tances may belong to the shortest class for the $\mathrm{P^V}$–tpp complexes. Although the coordination geometry around the phosphorus atom is nearly octahedral, the four porphinate nitrogen atoms are in an S_4 deviation from planarity. The atomic deviations of the nitrogen atoms range from ±0.018(3) to ±0.019(3) Å, and the phosphorus atom lies just in this nitrogen plane. The S_4 deviation is consistent with the above buckling.[15] In $[\mathrm{P(OH)_2(tpp)}]^+$, four nitrogen atoms are co-planar and the phosphorus atom is above this plane.

The N—C bond distances (average 1.393 Å) in the pyrrole rings are significantly longer than those of the free ligand (average 1.369 Å).[16] The average of the $\mathrm{C_\alpha}$—$\mathrm{C_\beta}$ [e.g. C(1)—C(2)] bond distances in the same rings is 1.398 Å, which is substantially shorter than that of the free ligand (1.442 Å). However, no difference in the $\mathrm{C_\beta}$—$\mathrm{C_\beta}$ [e.g. C(2)—C(3)] bond distances has been observed between the coordinated and free ligand; averages are 1.353 and 1.351 Å, respectively. The average of the corresponding N—C bond distances in $\mathrm{P(OH)_2(tpp)](OH)\cdot 2H_2O}$ is 1.380 Å, which is in the middle of those in the present complex and free ligand.

The S_4 deviation of the nitrogen atoms makes the macrocycle ruffle, so that the dihedral angles between the nitrogen plane and respective pyrrole planes are enlarged to 31.2–32.9° (average of 32.1°) from 24.8–29.3° (average of 26.6°) in

Table 4. Dihedral angles (°) between selected planes and torsion angles (°) around the C—C bonds connecting the phenyl groups to the *meso* carbon atoms

	Plane 1	Plane 2	Plane 3	Plane 4[a]
Plane 0 [N(1)-N(4)]	32.9	31.2	31.5	32.8
Plane 1 [N(1) pyrrole]		46.1	64.4	46.3
Plane 2 [N(2) pyrrole]			42.4	63.8
Plane 3 [N(3) pyrrole]				41.8
Torsion angle[b]				
C(4)—C(5)—C(21)—C(22)	67.6(5)	C(9)—C(10)—C(27)—C(28)		−60.9(5)
C(4)—C(5)—C(21)—C(26)	−112.0(4)	C(9)—C(10)—C(27)—C(32)		119.5(4)
C(6)—C(5)—C(21)—C(26)	61.2(5)	C(11)—C(10)—C(27)—C(32)		−51.7(5)
C(6)—C(5)—C(21)—C(22)	−119.2(4)	C(11)—C(10)—C(27)—C(28)		127.9(4)
mean	64	mean		−56
C(14)—C(15)—C(33)—C(34)	53.8(5)	C(19)—C(20)—C(39)—C(40)		−52.9(5)
C(14)—C(15)—C(33)—C(38)	−124.3(4)	C(19)—C(20)—C(39)—C(44)		124.6(4)
C(16)—C(15)—C(33)—C(38)	49.6(5)	C(1)—C(20)—C(39)—C(44)		−45.7(6)
C(16)—C(15)—C(33)—C(34)	−132.3(4)	C(1)—C(20)—C(39)—C(40)		136.9(4)
mean	52	mean		−49

[a] Plane 4 is defined by the N(4) pyrrole ring [N(4)-C(20)].

[b] The sign is positive if when looking from the second atom to the third atom a clockwise motion of the first atom would superimpose it on the fourth atom.

$[P(OH)_2(tpp)](OH) \cdot 2H_2O$. The ruffling of the porphyrin ring is also S_4 symmetric; the dihedral angles between the pyrrole rings *trans* to each other are 64.4° and 63.8°, and those between the ones in *cis* positions range from 41.8° to 46.3° (see Table 4). All these angles are larger by 7–10° than those in the above relevant complex. The mode of the torsion of the phenyl rings around the C—C bonds connecting the rings to the *meso* carbons is also of S_4 character (Fig. 2 and Table 4). This mode does not hold in the above complex, in which the mode is of C_4 character. This C_4 character may be attributed to the packing effects.

In $[P(OH)_2(tpp)](OH) \cdot 2H_2O$ the phosphorus atom is displaced 0.09 Å from the mean plane of the porphinate nitrogen atoms.[5] Three models have been presented to explain this displacement: (i) assumption of square-pyramidal geometry for the $[P(OH)(tpp)]^{2+}$ five-coordinated chromophore; (ii) attribution to hydrogen bonding; and (iii) peculiarity to tpp complexes with small central atoms, although the authors have noted that all three have some inadequacies. In the $[PCl_2(tpp)]Cl \cdot CH_2Cl_2$ crystal, the displacement has not been observed; the calculated displacement is 0.003(3) Å from the nitrogen plane, which is defined by the four nitrogen atoms. Thus, the present molecular structure is a counter-example for (iii). In the present case none of the chlorides has significant hydrogen bonding character, in view of the van der Waals radii of hydrogen and chlorine atoms of 1.20 and 1.75 Å, respectively.[14]

The chloride ion is located in narrow surroundings by C(2), C(3) and C(45); the interatomic distances of Cl(3)···C(2), Cl(3)···C(3) and Cl(3)···C(45) are 3.332(4), 3.524(4) and 3.53(1) Å, respectively. The former distance of 3.332 Å seems exceptionally short in view of van der Waals contact of 3.50 Å.[14] The distances between the chloride ion and the hydrogen atoms [H(1) and H(30)] attached to C(2) and C(45) are 2.82 and 2.55 Å, respectively. The latter distance may be ascribed to hydrogen bonding.

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