Figure 2, show a shortest intermolecular C···C distance of 4.0 Å and a shortest intermolecular C···O contact of 3.3 Å. No abnormal van der Waals distances occur.

Crystal and Molecular Structure of the Radical Perchloratotetraphenylporphinatozinc(II)

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Abstract: The X-ray crystal structure of the radical, perchloratotetraphenylporphinatozinc(II), has been determined by the heavy-atom method and refined to a final agreement factor, R = 0.073, for 2244 reflections greater than 3σ. The compound crystallizes in the space group $P2_1/c$, with a = 13.638 (4), b = 13.017 (5), c = 20.452 (8) Å, β = 107.63 (2)°, and Z = 4. The perchlorate group is covalently coordinated to the zinc with a Zn–O distance of 2.079 (8) Å, the shortest metal to oxygen (perchlorate) distance yet reported, and a Zn–O–Cl angle of 130.2 (5)°. Distances and angles within the porphyrin agree with those found for other metalloporphyrins. ESCA and ir data suggest that the molecule has an electronic distribution similar to that of neutral metalloporphyrins. Intermolecular interactions of the phenyl groups prevent the dimer formation observed in Zn or Mg octaethylporphyrin radicals. A model for these dimers is the recently proposed π-complex.

Zinc tetraphenylporphyrin (ZnTPP) is one of a number[1-4] of metalloporphyrins which possess the ability to undergo oxidation or reduction of the porphyrin moiety with apparently little or no change in the central metal substituent. Solution epr and optical investigations[5] of the singly oxidized species have affirmed the correctness of an assignment in which a single electron is removed from the highest filled molecular orbital (a_{2u}) of the porphyrin.

Notwithstanding the characterizations mentioned above, the X-ray determination of the ZnTPPClO₄ molecular structure was undertaken to answer the following questions. (1) The preference of zinc in the porphyrin complex to assume square-pyramidal five-coordinate geometry is satisfied in ZnTPP by neutral ligands such as water and pyridine.[6-8] Halides in solution with ZnTPP⁺· are known[9] to form 1:1 complexes and, in the absence of a stronger ligand, will perchlorate now assume the role of an axial ligand? (2) No evidence for dimer formation of ZnTPPClO₄ at low

temperatures or in the solid state is found from epr or optical data, yet the analogous cation radicals of octaethylporphyrin Zn(II) or Mg(II) as the ClO_4^- or Br^- salts dimerize easily.[5,10] Can the phenyl rings sterically restrict dimer formation? (3) Does removal of a bonding electron affect significantly the molecular structure of the ring? (4) Are the physical properties of this model porphyrin radical, *i.e.*, crystalline order and stability to X-ray irradiation, well-behaved enough to attempt a similar study of the bacteriochlorophyll cation radical?

Experimental Section

ZnTPP was prepared by Adler's method.[11] The supporting electrolyte, tetra-*n*-propylammonium perchlorate, $(Pr)_4N^+ClO_4^-$, was synthesized using the procedure of House.[12] Dichloromethane was fractionally distilled from CaH₂ and stored over molecular sieves. Hexane was fractionally distilled and stored over molecular sieves.

The previously reported synthesis of ZnTPPClO₄ was modified slightly. A 0.1 M solution of $(Pr)_4N^+ClO_4^-$ in CH₂Cl₂ was swept with argon and preelectrolyzed at +1.20 V *vs.* sce (aq) to remove oxidizable impurities. When a base current was reached, approximately 30 mg of ZnTPP was added to the electrolysis cell and controlled potential oxidation proceeded at +0.80 V until the base cell current was reached. The potential was then raised to +0.85 V until the base current again was obtained. This sequence avoided demetalation of ZnTPP. The anolyte was transferred to a rotary evaporator and reduced to dryness. The residue was extracted with three 15-ml aliquots of benzene, and the combined solutions were filtered to remove supporting electrolyte. After taking the filtrate to

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dryness the product was observed to contain traces of ZnTPP and $(Pr)_4N^+ClO_4^-$.

Crystals suitable for diffraction studies were obtained by a combination of diffusion and evaporation of a layer of hexane floated on a CH_2Cl_2 solution of ZnTPPClO$_4$. The solution was left in the dark until most of the liquid had evaporated. The solid was washed with hexane, and ZnTPPClO$_4$ was separated manually from the $(Pr)_4N^-ClO_4^-$ impurity. *Anal.* Calcd for $C_{44}H_{28}N_4C_4ZnCl$: C, 67.87; H, 3.63; Cl, 4.56; N, 7.20. Found: C, 67.65; H, 4.04; Cl, 4.57; N, 7.30.

Crystallographic Data Collection. Crystals were mounted on glass fibers with epoxy glue and photographed using Ni-filtered Cu Kα radiation. Two monoclinic forms, both exhibiting similar tabular morphology, were observed. Precession photographs of the 0*kl*, 1*kl*, *h*0*l*, and *h*1*l* reciprocal lattice levels of the α form revealed lattice symmetry 2/*m* and systematic absences 0*k*0 (k = $2n$ + 1) and *h*0*l* (l = $2n$ + 1), uniquely defining the monoclinic space group $P2_1/c$ (no. 14).[13] Approximate cell constants and densities for the α form are a = 9.82 (1) Å,[14] b = 14.7 (1) Å, c = 24.9 (1) Å, β = 82.8 (2)°, V = 3560 Å^3, and ρ_{calcd} = 1.46 g cm^{-3}. Examination of precession photographs of the *h*k0 and 0*kl* reciprocal lattice levels and the full diffractometer data set (*vide infra*) of the β form revealed Laue symmetry 2/*m* and systematic absences 0*k*0 (k = $2n$ + 1) and *h*0*l* (l = $2n$ + 1), again indicating space group $P2_1/C$ (no. 14). The β form was used for data collection since crystal quality was generally superior to that of the α form.

A well-formed tabular crystal of the β form was mounted parallel to the b^* axis on a glass fiber and placed on a Picker four-circle automated diffractometer. Sixteen reflections at diverse setting angles were manually centered and used to refine cell parameters by a least-squares procedure. The cell parameters obtained were a = 13.638 (4) Å, b = 13.017 (5) Å, c = 20.452 (8) Å, β = 107.63 (2)°, and V = 3460 Å^3. The calculated density of 1.49 g cm^{-3} for four formula units per unit cell agrees with the experimental density of 1.45 g cm^{-3} measured for the mixture of α and β forms by the flotation method using a mixture of carbon tetrachloride and hexane. With four formula units per cell, there is no symmetry imposed on the structure by space group requirements and the asymmetric unit consists of one ZnTPPClO$_4$ formula unit.

Intensity measurements were made using Zr-filtered Mo radiation, with source-crystal and crystal-counter distances of 21 and 26 cm, respectively. The takeoff angle was adjusted to 1.3°, at which point the peak height of a typical medium intensity reflection was reduced to 90% of its maximum value. The width at half-height of ω scans of several typical medium reflections (*ca.* 10°) indicated a satisfactory mosaic spread for the crystal.[15] Using a scan rate of 1° min^{-1}, a symmetrical scan of 2° was taken about the calculated position (λ 0.7093 Å) for each reflection, and stationary background counts of 20 sec were taken at the beginning (*bgd*1) and at the end (*bgd*2) of the scan. Since the counting rate did not exceed 10^4 counts sec^{-1}, attenuators were not used during data collection. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak. Three reflections occurring in diverse regions of reciprocal space (400, 040, and 018) and a null reflection (070) were measured after every 100 reflections as a check on crystal and instrument stability. During data collection the standards decreased linearly by 5% and a correction was applied during data processing. Intensities (*I*) were obtained by subtracting three times the total measured background from the total integrated peak count (*CT*)

$$I = CT - 0.5(tc/tb)(bgd1 + bgd2)$$

where *tc* is the scan time and *tb* is the counting time of each background (either *bgd*1 or *bgd*2). The intensities were assigned standard deviations according to the formula[16]

$$\sigma(I) = [CT + 4.5 + 0.25(tc/tb)^2(bgd1 + bgd2 + 9.0) + (pI)^2]^{1/2}$$

Approximately 6400 reflections including several hundred sym-

metry equivalent reflections were collected in a complete quadrant of data out to 2θ = 50°. Practically no reflections with significant intensity were observed at or beyond this 2θ limit. After averaging equivalent reflections, 2244 unique reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.33 with p = 0.03. Corrections for Lorentz and polarization corrections were made in the usual way. The ten crystal faces were identified by optical means as the following (perpendicular distances in millimeters from the crystal center to the faces are given in parentheses): 001 (0.065), 00$\bar{1}$ (0.098), 011 (0.098), 00$\bar{1}$ (0.078), 0$\bar{1}$1 (0.078), 0$\bar{1}\bar{1}$ (0.239), 30$\bar{2}$ (0.239), $\bar{3}$02 (0.177), 110 (0.177), 110 (0.200). Absorption corrections were applied by the Gaussian quadrature method; corrections to F^2 ranged from 1.10 to 1.44.

Solution and Refinement of the Structure. Computations were performed using standard programs.[17] For structure factor calculations the scattering factors were taken from Cromer and Waber's tabulation[18] for all atoms except hydrogen. Stewart's hydrogen atom scattering factors were used.[19] The scattering factors for zinc and chlorine were corrected for the real and imaginary anomalous dispersion components, using the dispersion factors given by Cromer.[20] The agreement factors are defined in the usual way as

$$R = (\sum||F_o| - |F_c||)/(\sum|F_o|)$$

and

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$.

A three-dimensional Patterson synthesis based on 1215 low-angle reflections revealed trial coordinates for zinc, chlorine, and one nitrogen. The remaining carbon, nitrogen, and oxygen atoms were located in a straightforward manner with a series of Fourier syntheses and least-squares refinements. The four phenyl groups were refined as groups with fixed geometry (D_{6h} symmetry, C–C = 1.373 Å); the rigid group approximation was used both because the number of structure variables would be more limited and because the structure of the phenyl groups would in all likelihood be more accurately known from the numerous previous determinations than could be determined in the present structure. Hydrogen atoms were included in periodically updated calculated positions (C–H = 0.95 Å)[21] for the eight pyrrole and 20 phenyl positions. Temperature factors were taken as (B + 1) where B is the isotropic temperature factor of the atom or group to which the hydrogen is bonded.

Least-squares refinement, employing a weighting scheme based on counting statistics (w = $4I/\sigma(I)^2$), varying an overall scale factor, individual positional and anisotropic temperature factors for the 25 nongroup atoms, and seven variables (three orientation angles, three positional parameters, and an overall group temperature factor) for each of the four groups, converged to give the residuals R = 0.0838 and R_w = 0.0728 (2244 observations, 300 variables). In the final refinement no parameter shifted more than one estimated standard deviation from the previous value. The maximum shift in the final cycle was 0.09 standard deviation (β_{11} for oxygen atom O4) and the error in an observation of unit weight was 0.83. A final difference Fourier synthesis contained as the major feature a peak near the interior of phenyl group B of height 0.77 e Å^{-3}, which compares with a value near 2.00 e Å^{-3} for a typical carbon atom in this structure. A detailed analysis of the function $\sum w(||F_o| - |F_c||)^2$ for various combinations of indices, ranges of $\lambda^{-1} \sin \theta$, and magnitudes of structure factors revealed no unusual trends, thus supporting the weighting scheme chosen. Final positional and thermal parameters are given in Tables I and II. A list of calculated and observed structure factors is available.[22]

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(14) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

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(22) See paragraph at end of paper regarding supplementary material.

Table I. Individual Atomic and Thermal Parameters for the Nongroup Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.2460 (1)	0.0974 (1)	0.0288 (1)	0.0030 (1)	0.0035 (1)	0.00134 (4)	0.0006 (1)	0.00019 (4)	−0.0001 (1)
Cl	0.2556 (2)	0.2558 (4)	−0.0955 (2)	0.0045 (2)	0.0097 (4)	0.0043 (2)	0.0006 (2)	0.0006 (2)	0.0036 (2)
O1	0.3261 (8)	0.2987 (9)	−0.1232 (6)	0.0081 (8)	0.0127 (13)	0.0066 (6)	0.0029 (8)	0.0042 (5)	0.0053 (7)
O2	0.2274 (13)	0.3398 (13)	−0.0525 (10)	0.0185 (17)	0.0122 (15)	0.0131 (12)	0.0051 (13)	0.0092 (12)	0.0021 (10)
O3	0.3035 (6)	0.1775 (8)	−0.0455 (5)	0.0057 (6)	0.0071 (9)	0.0037 (4)	−0.0004 (6)	0.0023 (4)	0.0025 (5)
O4	0.1629 (9)	0.2305 (12)	−0.1365 (7)	0.0109 (10)	0.0168 (17)	0.0048 (5)	−0.0035 (10)	−0.0013 (6)	0.0025 (7)
N1	0.1789 (6)	−0.0243 (8)	−0.0425 (5)	0.0035 (6)	0.0034 (8)	0.0019 (3)	0.0006 (5)	0.0003 (4)	−0.0008 (4)
N2	0.3706 (6)	0.0025 (7)	0.0653 (4)	0.0024 (5)	0.0036 (9)	0.0019 (3)	0.0026 (5)	−0.0006 (3)	0.0009 (4)
N3	0.2942 (6)	0.1892 (8)	0.1100 (5)	0.0037 (6)	0.0031 (8)	0.0013 (3)	−0.0001 (5)	0.0007 (3)	−0.0003 (4)
N4	0.1024 (6)	0.1632 (8)	0.0018 (4)	0.0017 (5)	0.0061 (9)	0.0012 (3)	0.0013 (5)	0.0001 (3)	0.0005 (4)
C1	0.0861 (8)	−0.0147 (10)	−0.0928 (6)	0.0033 (7)	0.0043 (11)	0.0018 (4)	−0.0008 (7)	0.0004 (5)	0.0003 (5)
C2	0.0827 (7)	−0.0921 (12)	−0.1429 (6)	0.0040 (7)	0.0055 (11)	0.0026 (5)	0.0016 (9)	0.0000 (4)	0.0018 (7)
C3	0.1724 (9)	−0.1493 (11)	−0.1204 (6)	0.0069 (9)	0.0056 (12)	0.0017 (4)	0.0004 (8)	0.0011 (5)	−0.0011 (5)
C4	0.2288 (7)	−0.1078 (11)	−0.0568 (6)	0.0041 (7)	0.0032 (9)	0.0023 (4)	−0.0007 (7)	0.0016 (4)	0.0001 (6)
C5	0.3271 (8)	−0.1405 (9)	−0.0169 (6)	0.0036 (7)	0.0040 (11)	0.0019 (4)	0.0005 (6)	0.0012 (4)	0.0005 (5)
C6	0.3887 (7)	−0.0906 (13)	0.0427 (6)	0.0035 (7)	0.0064 (12)	0.0025 (4)	0.0005 (9)	0.0001 (4)	0.0006 (7)
C7	0.4774 (9)	−0.1386 (10)	0.0898 (7)	0.0060 (10)	0.0032 (11)	0.0024 (5)	0.0016 (7)	−0.0001 (5)	−0.0009 (6)
C8	0.5125 (8)	−0.0670 (10)	0.1389 (6)	0.0057 (8)	0.0050 (13)	0.0016 (4)	−0.0003 (7)	0.0004 (4)	0.0007 (5)
C9	0.4483 (8)	0.0205 (9)	0.1244 (6)	0.0029 (7)	0.0025 (9)	0.0027 (5)	0.0002 (6)	0.0009 (5)	0.0012 (5)
C10	0.4603 (7)	0.1101 (10)	0.1658 (5)	0.0054 (8)	0.0032 (11)	0.0013 (3)	0.0002 (8)	0.0003 (4)	0.0005 (5)
C11	0.3888 (9)	0.1894 (10)	0.1549 (6)	0.0045 (8)	0.0053 (12)	0.0016 (4)	0.0010 (7)	−0.0002 (4)	0.0000 (5)
C12	0.4040 (8)	0.2812 (10)	0.1965 (7)	0.0041 (8)	0.0073 (14)	0.0026 (5)	0.0000 (8)	−0.0004 (5)	−0.0021 (6)
C13	0.3157 (9)	0.3332 (10)	0.1766 (6)	0.0053 (9)	0.0048 (12)	0.0017 (4)	0.0001 (8)	−0.0006 (4)	−0.0013 (5)
C14	0.2463 (9)	0.2750 (10)	0.1268 (6)	0.0058 (9)	0.0041 (12)	0.0022 (4)	0.0012 (8)	0.0015 (5)	−0.0007 (6)
C15	0.1418 (8)	0.2961 (10)	0.0907 (6)	0.0035 (7)	0.0058 (12)	0.0012 (3)	0.0008 (7)	0.0008 (4)	0.0006 (5)
C16	0.0779 (7)	0.2404 (10)	0.0373 (5)	0.0038 (7)	0.0038 (11)	0.0013 (4)	0.0017 (7)	0.0009 (4)	0.0003 (5)
C17	−0.0302 (7)	0.2599 (10)	0.0124 (6)	0.0024 (6)	0.0057 (12)	0.0018 (4)	0.0010 (7)	0.0004 (4)	−0.0009 (5)
C18	−0.0678 (8)	0.1923 (11)	−0.0373 (7)	0.0037 (8)	0.0054 (13)	0.0026 (5)	0.0004 (5)	0.0008 (5)	0.0014 (6)
C19	0.0164 (7)	0.1331 (9)	−0.0454 (5)	0.0039 (7)	0.0041 (10)	0.0009 (4)	−0.0006 (6)	0.0007 (4)	0.0006 (5)
C20	0.0084 (8)	0.0553 (9)	−0.0933 (6)	0.0040 (8)	0.0039 (11)	0.0016 (4)	0.0021 (7)	0.0011 (4)	0.0008 (5)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$.
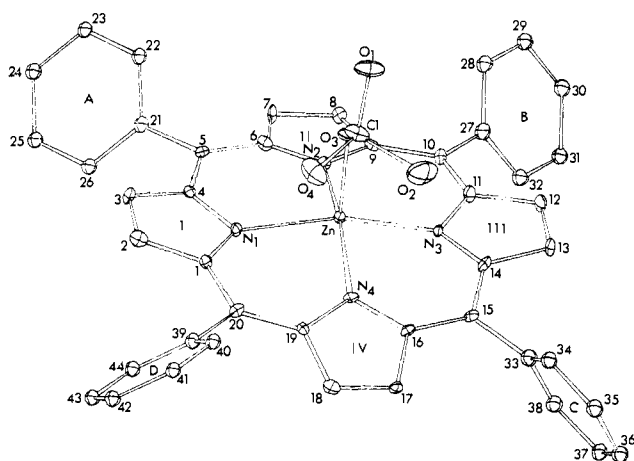
Figure 1. Numbering scheme for the tetraphenylporphyrin moiety. Hydrogen atoms, not shown, bear the same number as the carbon atom to which they are bonded. Thermal ellipsoids are drawn at 50% probability.

Discussion

Bond distances and angles are given in Tables III and IV, in accord with the numbering scheme presented in Figure 1. Deviations from the least-squares plane of the porphyrin skeleton are listed in Table V. Although departures of the porphyrin ring from planarity are large, individually the pyrrole rings II, III, and IV are planar to within 0.017 Å and ring I to within 0.025 Å. The four nitrogens are planar to within 0.003 Å and the dihedral angles between this plane and pyrrole rings I, II, III, and IV are 10.1 (10), 15.7 (9), 4.7 (11), and 13.7 (9)°, respectively. Figure 1 displays the domed character of the porphyrin and additionally illustrates the coordinated perchlorate.

Table II. Derived Atomic Coordinates and Group Temperature Factors for the Phenyl Rings

Atom	Ring	x	y	z	B, Å²
C21	A	0.3602 (6)	−0.2446 (5)	−0.0345 (5)	3.8 (1)
C22		0.4557 (6)	−0.2540 (6)	−0.0433 (4)	
C23		0.4889 (5)	−0.3479 (7)	−0.0586 (4)	
C24		0.4265 (6)	−0.4325 (5)	−0.0653 (5)	
C25		0.3309 (5)	−0.4232 (6)	−0.0566 (4)	
C26		0.2978 (4)	−0.3292 (7)	−0.0412 (4)	
C27	B	0.5516 (5)	0.1113 (15)	0.2277 (3)	4.4 (1)
C28		0.6495 (6)	0.1062 (8)	0.2225 (4)	
C29		0.7327 (4)	0.1100 (13)	0.2805 (4)	
C30		0.7181 (5)	0.1189 (15)	0.3438 (3)	
C31		0.0202 (6)	0.1241 (7)	0.3490 (3)	
C32		0.5370 (4)	0.1203 (12)	0.2910 (4)	
C33	C	0.0990 (10)	0.3815 (9)	0.1223 (5)	4.4 (1)
C34		0.0869 (9)	0.3652 (7)	0.1857 (5)	
C35		0.0324 (6)	0.4341 (7)	0.2118 (3)	
C36		−0.0101 (10)	0.5195 (9)	0.1745 (5)	
C37		0.0020 (9)	0.5358 (7)	0.1110 (5)	
C38		0.0565 (6)	0.4669 (7)	0.0850 (3)	
C39	D	−0.0884 (5)	0.0473 (7)	−0.1525 (3)	4.0 (1)
C40		0.1370 (6)	−0.0458 (6)	−0.1688 (4)	
C41		−0.2260 (6)	−0.0531 (5)	−0.2226 (4)	
C42		−0.2665 (5)	0.0328 (7)	−0.2601 (4)	
C43		−0.2190 (6)	0.1259 (6)	0.2437 (4)	
C44		−0.1289 (6)	0.1332 (6)	−0.1900 (4)	

In agreement with previous studies of metalloporphyrins, the phenyl ring dihedral angles of 53.9 (10), 57.9 (10), 68.4 (10), and 49.8 (10)° for rings A–D with planes formed from the meso carbon, C_m, and the neighboring pyrrole C_α atoms indicate only minor electronic conjugation with the porphyrin. This conclusion is supported by both the C_m to phenyl carbon bond lengths, 1.48 (1)–1.51 (1) Å, which are characteristic of σ bonding, and the small phenyl hydrogen hyperfine coupling constants previously reported.[5] In-

Table III. Selected Interatomic Bond Distances (Å)

Zn–N1	2.094 (9)			C1–C2	1.43 (2)		
Zn–N2	2.067 (8)	Zn–N	2.076 (9)ᵃ	C3–C4	1.40 (2)		
Zn–N3	2.082 (9)			C6–C7	1.44 (2)		
Zn–N4	2.061 (8)			C8–C9	1.41 (2)		
Zn–O3	2.079 (8)			C11–C12	1.45 (2)	C_a–C_b	1.43 (1)
Cl–O1	1.374 (10)			C13–C14	1.46 (2)		
Cl–O2	1.525 (17)			C16–C17	1.43 (1)		
Cl–O3	1.451 (9)			C18–C19	1.43 (2)		
Cl–O4	1.328 (11)						
N1–C1	1.37 (1)			C4–C5	1.41 (1)		
N1–C4	1.36 (1)			C5–C6	1.41 (2)		
N2–C6	1.35 (2)			C9–C10	1.42 (2)		
N2–C9	1.36 (1)	C_a–Nᵇ	1.35 (1)	C10–C11	1.39 (2)		
N3–C11	1.34 (1)			C14–C15	1.40 (1)	C_a–C_m	1.40 (1)
N3–C14	1.35 (1)			C15–C16	1.38 (1)		
N4–C16	1.34 (1)			C19–C20	1.39 (1)		
N4–C19	1.33 (1)			C20–C21	1.39 (1)		
C2–C3	1.39 (2)			C5–C21	1.51 (1)		
C7–C8	1.35 (2)			C10–C27	1.48 (1)		
C12–C13	1.33 (2)	C_b–C_b	1.35 (2)	C15–C33	1.49 (1)	C_m–phenyl	1.50 (1)
C17–C18	1.32 (2)			C20–C39	1.50 (1)		

ᵃ Errors in parentheses are averaged deviations from the mean. ᵇ The notation C_a, C_b, and C_m is that introduced by Hoard.[8]

Table IV. Selected Angles (deg)

N1–Zn–N2	87.8 (3)			N1–C1–C2	107.1 (10)		
N1–Zn–N4	88.7 (3)			N1–C4–C3	109.8 (9)		
N2–Zn–N3	88.7 (3)			N2–C6–C7	111.4 (10)		
N3–Zn–N4	88.4 (3)			N2–C9–C8	108.4 (11)		
N1–Zn–O3	97.6 (4)			N3–C11–C12	110.0 (10)	N–C_a–C_b	109.4 (10)
N2–Zn–O3	98.8 (3)			N3–C14–C13	109.0 (10)		
N3–Zn–O3	101.7 (4)			N4–C16–C17	109.8 (9)		
N4–Zn–O3	100.3 (3)			N4–C19–C18	108.5 (10)		
N1–N2–N3	90.7 (3)			C1–N1–C4	108.6 (9)		
N1–N4–N3	90.6 (3)			C6–N2–C9	106.5 (8)		
N2–N3–N4	89.4 (3)			C11–N3–C14	107.6 (10)	C_a–N–C_a	107.6 (5)
N2–N1–N4	89.3 (4)			C16–N4–C19	107.8 (9)		
O1–Cl–O2	106.0 (9)			C1–C2–C3	108.1 (10)		
O1–Cl–O3	110.7 (6)			C2–C3–C4	106.2 (11)		
O1–Cl–O4	119.5 (8)			C6–C7–C8	103.7 (11)		
O2–Cl–O3	103.6 (8)			C7–C8–C9	110.0 (10)		
O2–Cl–O4	100.6 (10)			C11–C12–C13	106.4 (10)	C_a–C_b–C_b	106.9 (13)
O3–Cl–O4	114.2 (7)			C12–C13–C14	106.9 (11)		
Zn–O3–Cl	130.2 (5)			C16–C17–C18	105.9 (10)		
Zn–N1–C1	122.3 (8)			C17–C18–C19	107.9 (9)		
Zn–N1–C4	126.2 (7)			C3–C4–C5	125.5 (11)		
Zn–N2–C6	127.3 (7)			C5–C6–C7	122.6 (13)		
Zn–N2–C9	126.2 (8)			C8–C9–C10	125.7 (10)		
Zn–N3–C11	125.3 (8)	Zn–N–C_aᵃ	125.5 (7)ᵇ	C10–C11–C12	123.4 (10)		
Zn–N3–C14	125.0 (6)			C13–C14–C15	125.4 (11)	C_b–C_a–C_m	124.4 (12)
Zn–N4–C16	125.1 (7)			C15–C16–C17	121.7 (10)		
Zn–N4–C19	126.9 (8)			C18–C19–C20	125.4 (9)		
N1–C4–C5	124.5 (10)			C2–C1–C20	124.3 (10)		
N2–C6–C5	126.0 (10)			C4–C5–C6	125.2 (10)		
N2–C9–C10	125.9 (10)			C9–C10–C11	124.4 (9)		
N3–C11–C10	126.4 (11)			C14–C15–C16	124.1 (10)	C_a–C_m–C_a	124.7 (4)
N3–C14–C15	124.9 (11)	N–C_a–C_m	126.1 (8)	C19–C20–C1	125.0 (10)		
N4–C16–C15	128.6 (9)						
N4–C19–C20	126.1 (10)						
N1–C1–C20	126.2 (11)						

ᵃ The notation C_a, C_b, and C_m is that introduced by Hoard.[8] ᵇ Errors in parentheses are averaged deviations from the mean.

tramolecular contacts (other than bonding distances) less than 2.80 Å involve interactions between ortho phenyl hydrogens and β-carbon or β-hydrogen atoms on adjacent pyrrole groups. These contacts, as short as 2.26 Å (H44–H2) but more typically in the range 2.5–2.9 Å, restrict phenyl group rotation toward coplanarity with the porphyrin.

The perchlorate group functions as a tightly bound monodentate ligand (Figures 1 and 2). The Zn–O3 distance, 2.079 (8) Å, is to our knowledge the shortest metal–oxygen(perchlorate) distance reported and compares well to the sum of Zn (1.34 Å) and O (0.73 Å) covalent radii.[23] This distance also compares favorably to the values reported for Zn–OH₂, 2.00 Å, in Zn(acac)₂· H₂O[24] and for Zn–HOC₂H₅, 2.068 Å, in Zn(benzac)₂·

(23) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y., 1962.
(24) H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **16**, 748 (1963).

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Figure 2. Geometry about the Zn atom.

Table V. Atomic Deviations (Å) from Least-Square Planes

Atom	Porphyrin[a]	Individual pyrrole[b]	Atom	Porphyrin	Individual pyrrole
N1	−0.004	0.023	N3	0.101	0.002
C1	0.087	−0.014	C11	0.176	−0.008
C2	0.278	−0.002	C12	0.312	0.001
C3	0.249	0.017	C13	0.276	−0.009
C4	0.023	−0.025	C14	0.160	0.004
C5	−0.030		C15	−0.070	
N2	0.077	−0.017	N4	0.031	−0.010
C6	−0.092	0.017	C16	−0.161	0.001
C7	−0.440	−0.011	C17	−0.510	0.008
C8	−0.403	0.002	C18	−0.531	−0.014
C9	−0.077	0.009	C19	−0.150	0.015
C10	0.022		C20	−0.033	

[a] Plane includes 20 carbon atoms and four nitrogen atoms. [b] Plane includes only the five atoms composing the pyrrole.

HOC_2H_5.[25] First-row transition metal to monodentate perchlorate oxygen distances normally range[26–29] between 2.3 and 2.6 Å, although an early disordered structure yields[29] a value of 2.1 Å in $Co(Ph_2MeAsO)_4$-$(ClO_4)_2$. The angle at the coordinated oxygen atom, 130.2 (0.5)°, is normal for this type[25, 29] of coordination. The Zn–O distance, 2.079 (8) Å, is similar to an estimate[6] of $Zn-OH_2 = 2.06$ Å in the disordered ZnTPP-(H_2O) structure.

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(26) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, Abstracts, American Crystallographic Association, Spring Meeting, 1973.
(27) M. S. Hussain, M. D. Joesten, and P. G. Lenhart, Inorg. Chem., 9, 162 (1970).
(28) F. A. Cotton and D. L. Weaver, J. Amer. Chem. Soc., 87, 4189 (1965).
(29) P. Pauling, G. B. Robertson, and G. A. Rodley, Nature (London), 207, 73 (1965).

The perchlorate is oriented above the porphyrin ring in a striking fashion (Figure 1). The uncoordinated oxygen atoms are almost symmetrically situated above the porphyrin, and the pseudomirror plane of the perchlorate group is almost parallel to the N4–Zn–O3 plane, the dihedral angle between this plane and that formed by Zn–O3–Cl being 0.5 (3)°. The uncoordinated oxygen atoms O2 and O4 lie almost symmetrically over the two six-membered chelate rings formed with Zn, C_m, and pyrroles III and IV and I and IV, respectively. The shortest contacts between these oxygen atoms and porphyrin atoms are O4–N4 = 3.30 Å and O2–N3 = 3.25 Å, values in excess of the sum of the van der Waals radii for N and O (2.90 Å). If the perchlorate group is rotated approximately 45° about the Zn–O3 bond (maintaining the 130° angle for Zn–O3–Cl) so that the pseudomirror planes of the perchlorate group and six-membered chelated rings coincide, then O2–N4 and O4–N4 distances are minimized at the extremely small value of 2.1 Å. Thus the observed bisecting configuration for perchlorate minimizes repulsive interactions between uncoordinated oxygen atoms and pyrrole nitrogen atoms.

With one exception, no additional inter- or intramolecular distances less than 3.0 Å to the perchlorate are observed in this structure. An intermolecular contact of 2.48 Å between O2 and H25 (translated in the b direction) is slightly less than the sum of van der Waals radii[30] for O and H (2.60 Å). However, it is unlikely that the observed perchlorate conformation is forced by this one, weak contact.

Coordination reduces the perchlorate symmetry and causes splitting of the ClO_4 stretching band. Both the mull (Nujol) and solution (CH_2Cl_2) spectrum showed ν_{Cl-O} bands at 1100–1140 (vs, b) and 1022 (s) cm^{-1} with a band at 908 (w, b) cm^{-1} observed only in the mull. These positions agree with the previously reported[28, 31, 32] ir spectra of a monodentate perchlorate group. This experiment indicates appreciable coordination even in a CH_2Cl_2 solution.

Arrangement of atoms bonded to the Zn atom is that anticipated by consideration of the structural constraints discussed by Hoard.[7] Figure 2 displays distances and angles in this region. The nitrogens form the base of a square pyramid with the Zn situated 0.347 (9) Å above this plane a length not significantly distinct from the 0.33 Å out-of-plane displacement observed in tetra(4-pyridyl)porphinate zinc(II) pyridinate (PyZn-TPyP). This agreement persists upon comparison of the other structural parameters in this region. Averaged C–C bond lengths and angles (Tables III and IV) fall within the range of distances discussed by Hoard.[8] Comparison with PyZnTPyP shows that the porphyrin skeleton in $ZnTPPClO_4$ may have experienced slight contraction. However, the estimated standard deviations preclude correlation of bond length changes with bond order changes in the oxidized porphyrin. Nonetheless we can conclude that no appreciable structural changes have occurred.

(30) L. Pauling, "Nature of The Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.
(31) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed. Wiley-Interscience, New York, N. Y., 1970, pp 175–176.
(32) D. L. Lewis, Ph.D. Thesis, The University of North Carolina, Chapel Hill, N. C., 1973.

The molecular packing, Figure 3, consists of Zn-TPPClO$_4$ units isolated by normal van der Waals interactions. Except for a contact of 2.48 Å between H25 and O2, a contact of 2.49 Å between H36 and H2, and a contact of 2.71 Å between H35 and H2, no intermolecular contacts less than 2.84 Å are observed, and all other intermolecular contacts less than 3.0 Å involve phenyl hydrogen distances to glide-related asymmetric units.

Figure 3 exhibits one intriguing feature which merits further speculation. Pairs of ZnTPPClO$_4$ molecules crystallize about inversion centers to give "incipient dimers" with apparent π overlap between pyrroles IV on each porphyrin group. The centers of the inversion-related pyrrole groups IV are separated by some 5.19 Å (the separation between the IV pyrrole plane and the plane of the inversion-related porphyrin group is 3.84 Å). Phenyl groups adjacent to pyrroles IV are rotated away to form a pocket for closest approach of the pyrrole rings. A careful analysis of the molecular packing reveals no intermolecular contacts less than 3.0 Å but does indicate that closer approach of the two asymmetric units rapidly leads to serious phenyl–phenyl and phenyl–pyrrole interactions between hydrogen atoms on the two asymmetric units. Further rotation of the phenyl groups to provide a large pocket and closer approach of the pyrroles is prohibited by the already significant intramolecular ortho hydrogen pyrrole carbon or hydrogen contacts.

Thus, intermolecular contact of the phenyl groups with phenyl or pyrrole atoms provides a rationale for the nonobservance of cation radical dimers when TPP is the porphyrin moiety. On the basis of data presented here we surmise that the observed dimers of Mg or Zn octaethylporphyrin cation radicals will not be linked by a bridging anion (Br$^-$ or ClO$_4^-$), since there are no structural constraints in this configuration unique to the tetraphenylporphyrins. On the other hand, the π-complex structure advanced by Mauzerall, et al.,[10] is plausible for the octaethylporphyrins. This is easily envisioned from Figure 3 by removing the phenyl groups and permitting the asymmetric units composing the dimer to slide together. In this model interplanar spacing between the nitrogen planes is ~3.8 Å and the shortest distances, between β-pyrrole carbon atoms on different dimer moieties, is ~3.2–3.3 Å, separations slightly in excess of the sum of van der Waals radii. Dimer formation between (formal) cations is surprising, but the counterion, tightly bound to the metal, likely provides a source of compensating charge to the porphyrin ring.

Photoelectron X-ray spectroscopy provides information on atomic charge densities, and, in ZnTPP and ZnTPPClO$_4$, Zn and C inner shell binding energies are indistinguishable, while the N binding energies only differ by 0.4 ± 0.2 eV.[33] The similarity in charge distribution is at variance with the predictions of a π-electron theory[5] which yields differences of +0.1 esu for a meso carbon atom. Since the spin densities are accurately predicted by this theory, we suggest that the net charge distribution results primarily from electron density alterations in the molecular σ system.

The ability of the porphyrin ring to act as a source or sink of electron density as the axial ligand or metal

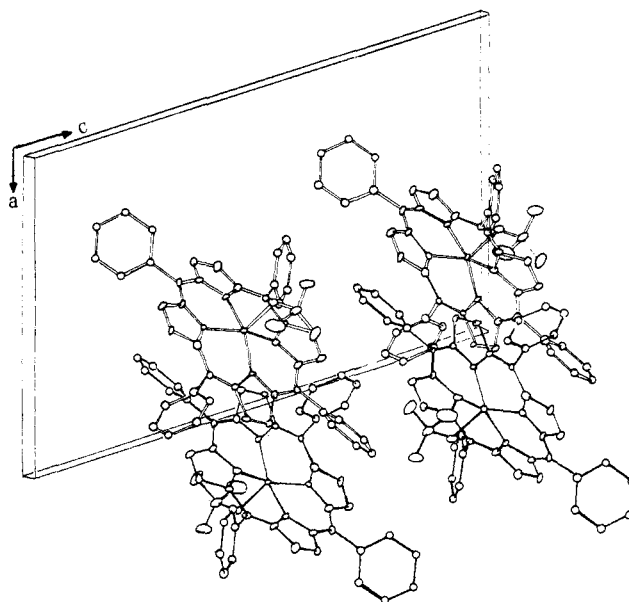(33) N. Winograd and D. H. Karewik, unpublished results.

Figure 3. The molecular packing of ZnTPPClO$_4$, viewed approximately perpendicular to the ac plane.

varies is not a novel suggestion. Gouterman,[34] much earlier, correlated both vibronic intensities and peak absorbances in metalloporphyrin Q-band spectra with the inductive changes in porphyrin electron density. In metallotetraphenylporphyrins bathochromic shifts and O–O Q-band intensity, increases are characteristic of increased electron density in the porphyrin, features displayed in the optical spectra of OH$^-$, Cl$^-$, and Br$^-$ complexes of ZnTPP.[35] This viewpoint thus suggests cations of other metalloporphyrins should bind perchlorate; indeed, the reported parent peak in the mass spectrum of octaethylporphyrin silver(III) perchlorate requires a coordinated perchlorate.[36] Interestingly, no parent peak was observed in the mass spectrum of ZnTPPClO$_4$; ZnTPP was the predominant species at high m/e.

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