

these experiments the total number of radicals generated ($4 \mu M$) was too small to affect the buffering capacity of the phosphate solutions, no pH shift occurred which could explain the change in k_{obsd} . The effect was also checked at pH 6.91 in the absence of buffers (see the Results section and Table II).

In view of these observations we assume for the present that complex reactions are involved despite the fact

that the observed decay follows strictly second-order kinetics.

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Crystal Structure of Nickel(II) Deoxyphylloerythrin Methyl Ester 1,2-Dichloroethane Solvate. A Carbocyclic Porphyrin

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Abstract: The crystal and molecular structure of nickel(II) deoxyphylloerythrin methyl ester 1,2-dichloroethane solvate, $C_{34}H_{36}N_4O_2Ni \cdot \frac{1}{2}C_2H_4Cl_2$, has been determined by three-dimensional X-ray techniques. Pertinent crystal data are: space group $P\bar{1}$, $a = 10.376$, $b = 11.749$, $c = 13.512 \text{ \AA}$, $\alpha = 90.70$, $\beta = 94.38$, $\gamma = 107.91^\circ$, $Z = 2$. The structure was determined by conventional Fourier techniques and refined by full-matrix least squares. The weighted R factor for 4295 reflections is 5.8% and the unweighted R factor is 11.2%. The porphyrin molecule is nearly planar, with a very slight ruffling effect. No local deviations from planarity were observed except for the atoms of the carbocyclic ring E. The nickel atom was found to lie in the plane of the molecule. As determined for the structure of vanadyl deoxyphylloerythroetioporphyrin, it was again noted that the distance between the metal atom and the nitrogen of ring C is shorter (1.89 \AA) than the other three metal-nitrogen distances ($\text{av} = 1.97 \text{ \AA}$). This shortening is probably due to the added strain introduced by the fifth carbocyclic ring E.

Geochemists and chemists have been investigating the relationship between chlorophyll and the tetraporphyrins since 1934 when Treibs isolated and identified etioporphyrin(III) (Etio) and deoxyphylloerythroetioporphyrin (DPEP) from various samples of natural bituminous materials including oil, shale, and coal.¹ Treibs proposed a scheme whereby, in geological time, hemin could be degraded to Etio and chlorophylls a and b to DPEP. Much work has been done since Treibs' proposal, and although the situation has been shown to be much more complex than he originally supposed, his ideas appear to be largely substantiated. An excellent introduction and review of this interesting area of geochemistry appears in a recently published book.²

As a further contribution to this area of chlorophyll-porphyrin chemistry, a series of X-ray analyses was undertaken at Mellon Institute designed to provide quantitative structural information on porphyrin and chlorin compounds which have conformational features in common with chlorophyll a. The structure of vanadyl-DPEP (VO-DPEP) was the first to be determined in this series.³ Nickel(II) deoxyphylloerythrin methyl ester (Ni-DPE), the second and current structure, is quite similar to VO-DPEP, but the methyl propionate side chain places it a step closer to the chlorophyll a molecule.

Experimental Section

Ni-DPE was prepared and isolated by E. W. Baker of this laboratory. The starting material was pheophytin a, which was degraded to deoxyphylloerythrin methyl ester.⁴ The two central hydrogen atoms were replaced by a nickel atom by refluxing the ester with nickel acetate in a 1:1 mixture of glacial acetic acid and dimethylformamide. Crystals were grown by a vapor-phase diffusion of methanol into a 1,2-dichloroethane solution of Ni-DPE at room temperature. The unit cell dimensions were determined from a least-squares refinement of accurately measured values of 2θ for 30 high-angle reflections. The presence of 0.5 mol of 1,2-dichloroethane was indicated by a density measurement and later confirmed by the solution of the structure. The density was determined by flotation in aqueous potassium iodide solution. Table I lists the pertinent crystallographic data.

Intensity measurements were made on an automated General Electric XRD-5 spectrogoniometer equipped with a NaI scintillation counter and pulse-height discriminator. The radiation employed was nickel-filtered copper and the takeoff angle from the X-ray tube was set at 0.04° . The θ - 2θ scan technique of Alexander and Smith was employed, using a variable scan range determined by the formula $2\theta_{\text{scan}} = 1.80 + 0.86 \tan \theta$.⁵ The scan rate was $2.0^\circ/\text{min}$. The reflection settings were generated by the program DIFSET of the X-ray 67 system.⁶ All of the generated reflections were stored on a magnetic tape and pulled off in groups of about 350 each using a program DATAPE written by R. F. Stewart. The output from this program took the form of a punched paper tape containing all necessary instructions to drive the Datex control unit of the diffractometer. Backgrounds were counted for 10 sec at both the high- and low-angle extremes of the scan range. An entire

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Table I. Crystallographic Data for Ni-DPE
1,2-Dichloroethane Solvate

Triclinic, $P\bar{1}$	$Z = 2$
$a = 10.376 (2) \text{ \AA}$	Empirical formula $C_{34}H_{36}N_4O_2Ni \cdot 1/2 C_2H_4Cl_2$
$b = 11.749 (2) \text{ \AA}$	Mol wt = 639.87
$c = 13.512 (2) \text{ \AA}$	$D_m = 1.355 \text{ g cm}^{-3}$
$\alpha = 90.78 (2)^\circ$	$D_x = 1.355 \text{ g cm}^{-3}$
$\beta = 94.38 (2)^\circ$	$F(000) = 674$
$\gamma = 107.91 (1)^\circ$	$\mu = 19.43 \text{ cm}^{-1}$ for Cu K α radiation
$V = 1561.6 \text{ \AA}^3$	$\mu l = 0.48$ for longest crystal dimension (Cu K α radiation)
Cu K α 1.5418 \AA	Limit of data collection: $\sin \theta/\lambda \leq 0.562 \text{ \AA}^{-1}$
Prominent crystal faces 100, 010, 001, 101	No. of data = 4295
Crystal size $0.25 \times 0.21 \times 0.06 \text{ mm}$	

were done on an IBM 360 computer at the Carnegie-Mellon University Computation Center. The least-squares program employed was that of Prewitt (SFLS-5),¹⁰ and the Fourier program was that of Zalkin (FORDAP),¹¹ both unpublished.

Solution and Refinement

The structure was solved by the heavy-atom technique. Fractional atomic coordinates were determined for the nickel atom by means of a sharpened Patterson map. This was followed by a difference Fourier map which revealed reasonable positions for the remaining atoms of carbon, nitrogen, oxygen, and chlorine. Positional and thermal parameters for all the atoms (43 excluding hydrogen) were refined by full-matrix least squares. These calculations included the entire data set, a total of 4295 reflections. The

Table II. Least-Squares Refinement of Ni-DPE

Cycle ^a	Atoms refined	Atoms not refined, but included in the structure factor calculations	Agreement, % W ^b	U ^c
1-3*	43 atoms. All were assigned isotropic B 's, except Ni, Cl, C(30)-C(33), O(1), and O(2), which were assigned anisotropic β 's	None	9.5	14.1
4*	Same	23 isotropic hydrogen atoms	8.2	13.4
5-6	Same	33 isotropic hydrogen atoms	6.7	12.0
7-8	Ni, N(A)-N(D), C(1)-C(24), C(28), and C(29). All were assigned anisotropic β 's	Cl, C(25)-C(27), C(30)-C(35), O(1), O(2), and 33 isotropic hydrogen atoms	6.1	11.6
9-10	C(2), C(3), C(5), C(7), C(8), C(10), C(12)-C(34), O(1), and O(2). All with anisotropic β 's	Ni, Cl, N(A)-N(D), C(1), C(4), C(6), C(9), C(11), C(35), and 33 isotropic hydrogen atoms	5.9	11.4
11	Ni, N(A)-N(D), C(1)-C(20), C(28), and C(29), all anisotropic	Cl, C(21)-C(27), C(30)-C(35), O(1), O(2) and 33 isotropic hydrogen atoms	5.9	11.4
12-16*	Cl, C(35), both anisotropic	All atoms of the porphyrin molecule	5.8	11.2

^a An asterisk indicates that the last cycle was followed by a Fourier difference map. ^b Weighted. ^c Unweighted.

hemisphere of reciprocal lattice points was measured for $2\theta \leq 120^\circ$, or $\sin \theta/\lambda \leq 0.562 \text{ \AA}^{-1}$. Three standard reflections were measured approximately once per hour to monitor the alignment and radiation damage of the crystal. There was no noticeable decrease in intensity for any of the standards during the course of the data collection. The raw intensity data were processed according to the scheme devised by Smith and Alexander.⁷ Relative structure factors (F_o) and their statistical variances (σ_{F_o}) were computed by this scheme. A reflection was classed as unobserved when $I_o \leq 1.5 \sigma(I_o)$, yielding 817 unobserved reflections out of a total of 4295 measured, nonequivalent reflections. For observed reflections

$$\sigma_{F_o} = 1/2 \sigma_{I_o} (LpI_o)^{-1/2}$$

and for unobserved reflections

$$\sigma_{F_o} = 1/2 F_o / 1.5 = 1/3 F_o$$

where F_o is a "threshold" value and is computed from the formula

$$F_o = \{ [1/(Lp)] 1.5 \sigma(I_o) \}^{1/2}$$

For the least-squares refinement, the function to be minimized was $\sum w(F_o - F_c)^2$, where the weights w are defined by $w = 1/\sigma_{F_o}^2$. No corrections were made for absorption, as the μl for the longest crystal dimension was less than 0.5.

The processed data were loaded onto magnetic tape with the program DATRDN of the X-ray 67 system.⁶ Scattering factors for neutral atoms were taken from Cromer and Waber,⁸ except for those of hydrogen, which were taken from Stewart, *et al.*⁹ The initial computing, which involved the solution of the structure, but not its refinement, was done on a CDC 1604A computer using the X-ray 67 system. The refinement and the hydrogen atom search

scattering contributions for nickel and chlorine were corrected for both the real and imaginary components of anomalous dispersion as given by Cromer ($\Delta f_{Ni}' = 3.2e$, $\Delta f_{Ni}'' = 0.67e$, $\Delta f_{Cl}' = 0.33e$, $\Delta f_{Cl}'' = 0.72e$).¹² The course of the refinement is briefly outlined in Table II.

Although positions for all of the hydrogen atoms could not be determined, a total of 33 was located from the difference maps computed after cycles 4 and 6. These atoms were assigned individual isotropic temperature factors of integral numerical values in such a way as to be about 1 \AA^2 greater than the temperature factor of the corresponding bonded carbon atom. Five of the hydrogen positions were observed to be associated with one of the methyl carbon atoms, C(27), each giving reasonable C-H bond distances and C-C-H bond angles. Since it is not unusual for a methyl group to have two or more orientations, each of these five atoms was assigned an occupation factor of 0.5 and included along with the other hydrogens in the structure factor calculations. A search was made in the final Fourier difference map for a sixth hydrogen, but it could not be found.

During the later stages of refinement, all of the non-hydrogen atoms were assigned anisotropic temperature factors, which raised the total number of parameters

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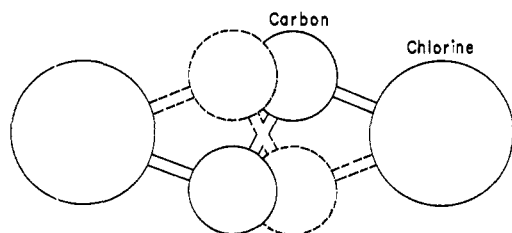


Figure 1. A qualitative perspective of the two energy-equivalent orientations for the solvent molecule of crystallization, 1,2-dichloroethane. The molecule lies on a symmetry center at $(\frac{1}{2}, 0, 0)$, and the two orientations share an axis which passes through the chlorine atom and the symmetry center.

to be refined to 388. Since the core size of the IBM 360 computer limited the refinement to 31 anisotropic atoms for a given cycle, the structure had to be refined in segments. Thus, the inner portion of the porphyrin molecule was refined for two cycles and then the outer portion for two cycles, with 21 of the atoms being refined in all four cycles. Finally, the inner part was refined again in cycle 11.

The final cycles (12–16), which refined only the solvent molecule, were not entirely satisfactory, as the carbon atom [C(35)] parameters did not converge. However, the maximum ratio of a C(35) atom parameter shift compared with the estimated error was 0.56, and no further refinement was attempted. If one considers all of the parameters that were refined in the structure, most of the ratios of the shift to estimated error were about 0.1–0.2 for the given parameter's last cycle of refinement. All of the ratios were less than 1.0 with the exception of one, the β_{22} for the nickel atom, which was 1.2. The final agreement factor is 5.8% using statistical weights, and 11.2% using unit weights.¹³

The Solvent Molecule

The 0.5 mol of 1,2-dichloroethane lies on a symmetry center and was shown by the refinement to occupy two energy-equivalent orientations. This became evident when both of the distinct carbon–chlorine distances refined to a value of slightly more than 2.1 Å, in agreement with the mean of the two carbon–chlorine distances of 1.49 and 2.63 Å observed in the low-temperature structure of 1,2-dichloroethane.¹⁴ Figure 1 is a qualitative perspective drawing which shows the two orientations. The plane of the drawing is meant to contain the two chlorine atoms, the center of symmetry (the intersection of the two C–C bonds), and the position to which the single carbon atom was refined. This latter position is not indicated in the drawing, but it would be located halfway between the pair of carbon atoms not related by the center of symmetry.

An attempt was made to locate positions for two half-carbon atoms by computing a Fourier difference map with the scattering contribution for the solvent carbon left out. However, a single peak appeared at the same position to which the atom had been pre-

(13) A table of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036 by referring to author, title of article, volume, and page number. Remit \$3.00 for photocopy or \$2.00 for microfiche. A copy may also be obtained by writing directly to the author.

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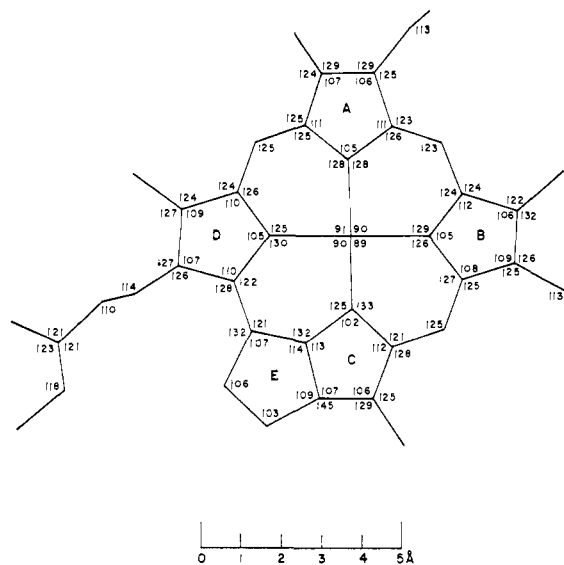
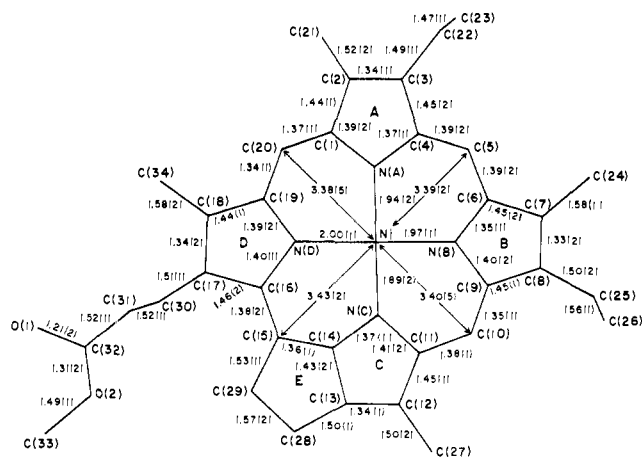


Figure 2. Intramolecular distances and angles for the Ni-DPE molecule based on the fractional coordinates listed in Table III. The least-squares estimated standard deviations for the distances are given in parentheses. The estimated standard deviations for the bond angles are all less than 1.0° and most are about 0.5° .

viously refined, and no further attempt was made to decompose this peak.

Results. Molecular Features and Crystal Packing

The refined fractional coordinates and anisotropic thermal parameters for the 43 nonhydrogen atoms are listed in the first part of Table III. The least-squares estimated standard deviations are given in parentheses and refer to the last significant figure. Fractional coordinates determined from a difference synthesis and isotropic temperature factors assigned as previously described are listed for 33 hydrogen atoms in the second part of Table III. The hydrogen atoms are numbered so as to correspond to the carbon atoms to which they are bonded. Figure 2 illustrates the numbering system used for the atoms and gives the values for the bond distances and angles based on the coordinates listed in Table III. The estimated standard deviations for the bond lengths are given in parentheses and refer to the last significant figure. The estimated standard deviations for the bond angles are all less than 1.0° , and most are about 0.5° . Table IV lists the carbon–hy-

Table III. Fractional Coordinates and Thermal Parameters for Ni-DPE

Heavy atoms	10 ⁴ x	10 ⁴ y	10 ⁴ z	10 ⁴ β ₁₁ ^a	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Ni	1327 (1)	3633 (1)	4846 (1)	75 (1)	46 (1)	47 (1)	13 (1)	0 (1)	0 (1)
O(1)	1215 (6)	8073 (5)	10106 (4)	267 (11)	127 (7)	113 (5)	28 (7)	21 (6)	-56 (5)
O(2)	-551 (5)	6429 (4)	9934 (4)	173 (8)	104 (6)	117 (5)	-6 (6)	51 (5)	-18 (4)
N(A)	2942 (4)	4530 (4)	4230 (3)	73 (7)	62 (6)	37 (4)	9 (5)	9 (4)	0 (4)
N(B)	1066 (5)	2281 (4)	3897 (3)	102 (7)	54 (6)	41 (4)	23 (5)	-10 (4)	-8 (4)
N(C)	-237 (5)	2735 (4)	5450 (4)	81 (7)	53 (5)	51 (4)	4 (5)	9 (4)	1 (4)
N(D)	1574 (5)	4986 (4)	5828 (3)	73 (7)	60 (6)	39 (4)	13 (5)	9 (4)	-8 (4)
C(1)	3796 (6)	5675 (6)	4494 (5)	80 (9)	57 (7)	42 (5)	-3 (6)	6 (5)	8 (5)
C(2)	4874 (6)	6024 (5)	3847 (5)	90 (9)	54 (7)	54 (5)	-4 (6)	10 (5)	0 (5)
C(3)	4694 (6)	5111 (6)	3188 (4)	97 (9)	76 (8)	53 (5)	18 (7)	25 (6)	6 (5)
C(4)	3486 (7)	4177 (6)	3432 (5)	100 (10)	68 (8)	52 (5)	18 (7)	-1 (6)	2 (5)
C(5)	2966 (6)	3090 (6)	2901 (5)	89 (9)	75 (8)	66 (6)	39 (7)	7 (6)	-4 (5)
C(6)	1814 (7)	2194 (6)	3138 (5)	107 (10)	71 (8)	49 (5)	33 (7)	11 (6)	-4 (5)
C(7)	1245 (7)	1064 (6)	2584 (5)	108 (10)	62 (7)	73 (6)	27 (7)	3 (6)	-21 (5)
C(8)	160 (7)	462 (5)	3036 (5)	117 (10)	47 (7)	61 (6)	4 (7)	-18 (6)	-17 (5)
C(9)	14 (7)	1188 (6)	3869 (5)	84 (9)	49 (7)	57 (5)	9 (6)	-4 (6)	-10 (5)
C(10)	-999 (7)	866 (6)	4477 (5)	93 (10)	56 (7)	62 (6)	-8 (7)	9 (6)	5 (5)
C(11)	-1158 (7)	1578 (6)	5249 (5)	98 (10)	60 (8)	52 (5)	13 (7)	-6 (6)	6 (5)
C(12)	-2220 (6)	1297 (6)	5932 (5)	78 (10)	85 (8)	56 (5)	17 (7)	1 (6)	8 (5)
C(13)	-1943 (6)	2249 (6)	6556 (5)	71 (9)	69 (8)	54 (5)	12 (7)	4 (5)	11 (5)
C(14)	-749 (6)	3117 (6)	6252 (5)	78 (9)	64 (7)	44 (5)	8 (7)	0 (5)	7 (5)
C(15)	-369 (6)	4173 (6)	6788 (4)	88 (9)	72 (8)	39 (5)	19 (7)	3 (5)	-2 (5)
C(16)	759 (6)	5097 (5)	6582 (4)	66 (8)	52 (7)	41 (5)	12 (6)	2 (5)	2 (4)
C(17)	1323 (6)	6268 (5)	7088 (4)	105 (10)	74 (7)	41 (5)	30 (7)	4 (5)	-2 (5)
C(18)	2448 (6)	6838 (5)	6650 (5)	89 (10)	75 (8)	50 (5)	30 (7)	1 (6)	5 (5)
C(19)	2610 (7)	6070 (6)	5858 (5)	98 (9)	59 (7)	44 (5)	23 (7)	-2 (5)	-6 (5)
C(20)	3609 (7)	6386 (6)	5245 (5)	78 (8)	73 (7)	44 (5)	3 (6)	6 (5)	-6 (5)
C(21)	5979 (6)	7234 (5)	3932 (5)	60 (9)	76 (7)	93 (6)	4 (6)	4 (6)	10 (5)
C(22)	5512 (7)	5036 (6)	2345 (5)	128 (11)	93 (8)	63 (6)	15 (7)	13 (6)	-2 (5)
C(23)	4958 (8)	5365 (7)	1400 (5)	273 (17)	224 (13)	54 (6)	31 (12)	20 (8)	20 (7)
C(24)	1865 (8)	780 (6)	1615 (5)	235 (14)	85 (8)	97 (7)	39 (9)	22 (8)	-43 (6)
C(25)	-772 (7)	-772 (5)	2744 (5)	121 (11)	61 (7)	87 (6)	15 (7)	4 (6)	-21 (5)
C(26)	-2017 (7)	-757 (6)	2022 (5)	126 (10)	118 (9)	96 (6)	16 (8)	-18 (7)	-23 (6)
C(27)	-3372 (6)	151 (5)	5902 (5)	126 (10)	57 (7)	81 (6)	-12 (7)	0 (6)	-10 (5)
C(28)	-2379 (6)	2751 (5)	7454 (5)	95 (9)	70 (7)	60 (5)	11 (6)	6 (5)	11 (5)
C(29)	-1378 (6)	4059 (5)	7577 (4)	106 (9)	80 (7)	50 (5)	27 (7)	13 (5)	3 (5)
C(30)	726 (6)	6750 (5)	7922 (4)	122 (9)	56 (7)	40 (4)	26 (6)	10 (5)	4 (4)
C(31)	1312 (6)	6570 (5)	8951 (5)	131 (10)	101 (8)	51 (5)	37 (7)	5 (6)	-6 (5)
C(32)	657 (9)	7087 (7)	9734 (5)	207 (14)	83 (9)	47 (5)	37 (9)	-12 (7)	-9 (5)
C(33)	-1291 (8)	6948 (7)	10621 (6)	259 (16)	167 (11)	117 (7)	84 (11)	114 (9)	-34 (7)
C(34)	3459 (6)	8130 (5)	6937 (5)	121 (10)	66 (7)	82 (6)	12 (7)	-21 (6)	10 (5)
Cl	4892 (2)	1757 (2)	102 (2)	235 (4)	226 (4)	214 (3)	30 (3)	-29 (3)	27 (3)
C(35)	4580 (19)	-120 (26)	258 (25)	331 (47)	295 (23)	467 (34)	88 (32)	82 (25)	53 (20)

Hydrogen atoms	10 ³ x	10 ³ y	10 ³ z	B, Å ²
H(5)	369	278	255	4.0
H(10)	-182	0	443	4.0
H(20)	471	713	536	4.0
H(21A)	674	703	359	5.0
H(21B)	548	775	360	5.0
H(21C)	674	737	468	5.0
H(22A)	556	398	230	5.0
H(22C)	642	537	252	5.0
H(23A)	539	567	55	9.0
H(23B)	500	609	142	9.0
H(23C)	413	488	117	9.0
H(24A)	155	-19	173	7.0
H(24B)	222	60	202	7.0
H(25A)	-24	-133	241	5.0
H(25B)	-140	-110	324	5.0
H(26A)	-156	-51	156	7.0
H(26B)	-241	-41	234	7.0
H(26C)	-272	-151	177	7.0
H(27A) ^b	-393	-17	514	5.0
H(27B) ^b	-350	-66	607	5.0
H(27C) ^b	-325	-77	547	5.0
H(27D) ^b	-341	2	678	5.0
H(27E) ^b	-422	41	581	5.0
H(28A)	-246	208	818	4.0
H(28B)	-315	293	723	4.0
H(29A)	-82	423	829	4.0
H(29B)	-183	481	752	4.0
H(30A)	94	763	780	4.0
H(30B)	-46	648	778	4.0
H(31A)	105	582	906	5.0
H(31B)	243	682	906	5.0
H(34A)	388	775	711	5.0
H(34B)	321	853	640	5.0

^a The β's as given in this table are introduced directly in the structure factor equation in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + \beta_{23}kl)]$. ^b Each of the five atoms H(27A)–H(27E) was assigned an occupation factor of 0.5, as explained in the text.

Table IV. Carbon-Hydrogen Bond Distances, Å

C(5)-H(5)	1.07	C(27)-H(27A)	1.14
C(10)-H(10)	1.11	C(27)-H(27B)	0.96
C(20)-H(20)	1.20	C(27)-H(27C)	1.27
C(21)-H(21A)	1.03	C(27)-H(27D)	1.20
C(21)-H(21B)	1.00	C(27)-H(27E)	1.02
C(21)-H(21C)	1.21	C(28)-H(28A)	1.26
C(22)-H(22A)	1.26	C(28)-H(28A)	0.92
C(22)-H(22B)	0.91	C(29)-H(29A)	1.07
C(23)-H(23A)	1.28	C(29)-H(29A)	1.12
C(23)-H(23B)	0.84	C(30)-H(30A)	1.00
C(24)-H(24A)	1.10	C(30)-H(30B)	1.17
C(24)-H(24B)	0.71	C(31)-H(31A)	0.85
C(25)-H(25A)	1.09	C(31)-H(31B)	1.10
C(25)-H(25B)	0.98	C(34)-H(34A)	0.74
C(26)-H(26A)	0.82	C(34)-H(34B)	0.93
C(26)-H(26B)	0.81		
C(26)-H(26C)	1.00	Av	1.04

drogen bond lengths. The average for the 33 carbon-hydrogen bond lengths is 1.04 Å, with a range of 0.71–1.28 Å.

A nuclear least-squares plane (NLS) was calculated using the coordinates for the 24 atoms of the porphyrin skeleton [N(A)–N(D), C(1)–C(20)]. The equation for this plane is $6.693x - 6.936y + 7.894z = 2.226$, where x , y , and z are fractional unit cell lengths. Table V

Table V. Displacements from the Best Least-Squares Plane Calculated from the Positions of Atoms N(A)–N(D) and C(1)–C(20)

	Displacement, Å		Displacement, Å
Ni	–0.00	C(15)	0.02
O(1)	–1.00	C(16)	0.04
O(2)	–0.77	C(17)	0.06
N(A)	–0.02	C(18)	0.02
N(B)	–0.01	C(19)	–0.00
N(C)	–0.01	C(20)	0.00
N(D)	–0.01	C(21)	–0.02
C(1)	–0.03	C(22)	0.03
C(2)	–0.03	C(23)	1.39
C(3)	–0.01	C(24)	0.19
C(4)	–0.01	C(25)	0.06
C(5)	0.01	C(26)	1.51
C(6)	0.01	C(27)	0.02
C(7)	0.06	C(28)	–0.09
C(8)	0.04	C(29)	0.02
C(9)	–0.01	C(30)	0.15
C(10)	–0.01	C(31)	–1.20
C(11)	–0.02	C(32)	–1.00
C(12)	–0.01	C(33)	–0.44
C(13)	–0.04	C(34)	–0.02
C(14)	–0.03		

lists the deviations in ångström units for each individual atom from this NLS plane. The results indicate the molecule to be slightly ruffled, which is a familiar feature of many porphyrin structures.^{15,16} Least-squares planes were also calculated for each of the five rings A–E, which are identified in Figure 2. The dihedral angles between each of these planes and the plane of the porphyrin skeleton are respectively -0.43 , 1.79 , -0.51 , 1.70 , and -2.26° . Local deviations from planarity for each of the pyrrole rings A–D were all found to be less than 0.01 Å, a feature also observed previously.^{15,16} Local deviations of the atoms from

(15) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, **87**, 2305 (1965).

(16) D. M. Collins and J. L. Hoard, *ibid.*, **92**, 3761 (1970).

the plane of the isocyclic ring E were understandably larger and ranged from $+0.03$ to -0.03 Å.

It is of interest to compare the planarity features of the Ni–DPE structure with those of similar X-ray structures. In the case of VO–DPEP,³ the vanadium atom is observed to be 0.54 Å out of the NLS plane of the porphyrin and 0.48 Å out of the NLS plane of the four nitrogen atoms. The displacement of the vanadium atom has the effect of “pulling” the nitrogen atoms out of the porphyrin plane, giving the entire molecule a shape much like that of a very shallow saucer. This has also been observed to a lesser extent for the structure of methoxyiron(III) mesoporphyrin IX dimethyl ester,¹⁷ where the iron(III) is 0.49 Å out of the best plane of the porphyrin molecule. The structure of $\alpha,\beta,\gamma,\delta$ -tetra(4-pyridyl)porphinatomonopyridinezinc(II) (ref 16) exhibits both an out-of-plane metal atom and a definite ruffle effect. The zinc(II) is 0.33 Å out of the best plane of the porphyrin toward the pyridine ligand. The molecule lies on a twofold axis, half of it making up the asymmetric unit of structure. The two nitrogens of the asymmetric unit are drawn 0.03 and 0.06 Å, respectively, out of the best porphyrin plane in the direction of the zinc(II) atom. Within the two pyrrole rings, the pairs of carbon atoms opposite the nitrogens are respectively 0.11, 0.13 Å and -0.17 , -0.17 Å out of the best porphyrin plane, indicating the ruffling effect.

The planarity pattern changes for chlorins, as indicated by the structure of methyl pheophorbide a (MePPb).¹⁸ A chlorin (green) has the same skeletal structure as a porphyrin (red), except that the partial double bond corresponding to C(18)–C(19) in Ni–DPE is a single bond. This has the effect of interrupting the continuous conjugated system that is common to porphyrins. MePPb is similar to chlorophyll a, but its long phytol chain has been replaced by a methyl group, and the magnesium atom has been replaced by two hydrogen atoms. The results of the MePPb X-ray analysis indicate that the rings corresponding to rings A, B, and C of Ni–DPE are each planar to within 0.01 Å, and ring E is planar to within 0.02 Å. As expected, ring D is not planar, the two carbon atoms opposite the nitrogen being 0.00 and 0.29 Å, respectively, out of the chlorin plane defined by atoms N(A)–N(D), C(1)–C(16), C(19), and C(20). Relative to the plane of the four nitrogen atoms, rings A and B are tipped up, while rings C, D, and E are tipped down.

The Ni–N(C) distance for Ni–DPE was observed to be shorter (1.89 Å) than the other three nickel–nitrogen distances (1.94, 1.97, and 2.00 Å), a feature that was also noted for the VO–DPEP and MePPb structures.^{3,18} If one compares the two distances between opposite nitrogen atoms, they calculate to be 3.83 Å [N(A)–N(C)] and 3.97 Å [N(B)–N(D)]. The corresponding distances are 3.96 and 4.08 Å for VO–DPEP, and 4.06 and 4.23 Å for MePPb. This effect appears to be due to the added strain of the carbocyclic ring E, as it is not observed for other similar structures where ring E is absent.

(17) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, **87**, 2312 (1965).

(18) M. S. Fischer, Ph.D. Thesis, University of California, Berkeley, Calif. 94720; Lawrence Radiation Laboratory Report No. UCRL-19524, 1969.

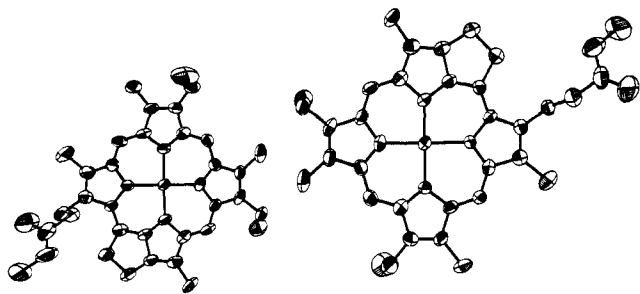


Figure 3. An ORTEP drawing of the unit cell contents projected onto the plane defined by the four nitrogen atoms of the right-hand molecule. The perspective is from a point directly above the nickel atom of the right-hand molecule and 24 in. from the plane of the paper.

Figure 3 is a computer-calculated ORTEP drawing of the unit cell contents excluding the hydrogen atoms and the solvent of crystallization.¹⁹ The molecule on the right side was constructed using the general atomic coordinates x, y, z as given in Table III. The left-hand molecule is equivalent and has the general coordinates $-x, -y, -z$. The perspective is along the vector perpendicular to the plane of the four nitrogen atoms of the right-hand molecule and intersects this plane at the nickel atoms. Each atom is drawn as a thermal ellipsoid based on the values of the refined anisotropic thermal parameters. The size of the thermal ellipsoids is such that there is a 50% probability that random points in a distribution function describing the atom's electron density will fall within the volume of the ellipsoid. For reasons of clarity, the solvent molecule of 1,2-dichloroethane was left out of this illustration. It fills space between the layers of porphyrin molecules and is positioned on the symmetry center at $(\frac{1}{2}, 0, 0)$.

The porphyrin molecules pack in parallel layers that coincide roughly with the $\bar{2}22$ crystallographic plane. The perpendicular spacing between the two molecules related by the center of symmetry at the origin is 4.46 Å. (This would be between the two molecules in Figure 3.) There are no intermolecular contacts, including the

(19) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoidal Plot Program for Crystal-Structure Illustrations," ORNL-3794, Oak Ridge, Tenn., 1965.

hydrogen atoms, which are less than 4.0 Å between these two molecules. The perpendicular spacing between the molecules related by the center of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is 3.47 Å. (The perpendicular separation between layers in graphite is 3.40 Å.) There are several intermolecular contacts of 4.0 Å or less for this pair of molecules and these distances are listed in Table VI along with all other distances less than 4.0 Å generated by other translational operators.

Table VI. Intermolecular Distances (Å) Less than 4.00 Å Excluding the Hydrogen Atoms

Operator x, y, z			
Cl-C(24)	3.77	C(35)-C(24)	3.89
Symmetry Operator $1 - x, 1 - y, 1 - z$			
Ni-C(21)	3.56	C(2)-C(4)	3.97
N(A)-C(1)	3.76	C(2)-C(20)	3.81
N(A)-C(2)	3.52	C(3)-C(19)	3.65
N(A)-C(21)	3.59	C(3)-C(20)	3.48
N(B)-C(21)	3.98	C(4)-C(20)	3.63
N(D)-C(22)	3.76	C(18)-C(22)	3.70
C(1)-C(1)	3.55	C(19)-C(22)	3.51
C(1)-C(2)	3.50	C(20)-C(22)	3.86
C(1)-C(3)	3.65	C(31)-Cl	3.93
C(1)-C(4)	3.78		
Translational Operator $1 + x, 1 + y, z$			
C(21)-C(25)	3.94	C(27)-C(34)	3.79
C(21)-C(26)	3.81		
Translational Operator $x, 1 + y, 1 + z$			
O(1)-C(24)	3.61	C(25)-C(33)	3.79
O(1)-C(35)	3.44	C(26)-C(33)	3.57
Translational Operator $1 + x, y, 1 + z$			
C(23)-C(33)	3.99		

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Correlation of Surface Tension between Various Liquids

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Abstract: A relationship between dielectric constant or index of refraction and surface tension has been found which correlates the surface tensions of diverse dielectric liquids. This seems to be the first such relationship discovered. It may be used to estimate the surface tension of non-hydrogen-bonded polar liquids and to obtain fairly accurate values of surface tension of nonpolar liquids.

There are many relationships in the scientific literature between the surface tension of a dielectric liquid and some other property of the liquid. How-

ever, there seems to be no relationship *between* the surface tensions of diverse liquids based upon some common physical property. We have found that such