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The Crystal and Molecular Structure of Vanadyldeoxophylloerythroetioporphyrin-1,2-dichloroethane Solvate: an Analogue of Chlorophyll*

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Single crystals of vanadyl deoxophylloerythroetioporphyrin-1,2-dichloroethane solvate, $C_{32}H_{34}N_4VO \cdot C_2H_4Cl_2$, were grown by a vapor-phase diffusion technique. Pertinent crystal data are: space group $P2_1/a$, $a = 17 \cdot 963$ (3), $b = 13 \cdot 961$ (1), $c = 14 \cdot 090$ (3) Å, $\beta = 116 \cdot 97$ (1)°, $Z = 4$. The structure was solved by locating the position of the vanadium atom from a three-dimensional Patterson map and calculating successive Fourier series to locate the remaining atoms. A difference map revealed positions for 28 of the 38 hydrogen atoms, and these were used in the refinement procedure. Full-matrix least-squares calculations gave a final weighted R of 5·5% for approximately 2000 observed and unobserved reflections. The interesting feature of this molecule is the effect of the fifth isocyclic ring, *E*, on the porphyrin skeleton. Results indicate that this ring introduces strain into the molecule and causes distortions in the bond angles and most likely causes a shortening of the V–N bond to the ring C atom from an average of 2·10 Å for the other three V–N bonds to 1·96 Å for the shortened bond. The carbon and nitrogen atoms of the porphyrin skeleton are relatively planar and the vanadium atom lies 0·48 Å out of the plane of the four nitrogen atoms.

Introduction

In recent years new insights have been gained into the structure of chlorophyll and its related compounds. The basic structure of chlorophyll was worked out in the late 1930's by Hans Fischer (Fischer & Wenderoth,

1940) and subsequently confirmed through a very elaborate synthesis by R. B. Woodward and associates (Woodward, 1961). The accumulation of chemical information has recently made possible the description of the absolute configuration of chlorophyll *a* (Fleming, 1967). Crystallographers have shown an interest in an accurate structure determination for chlorophyll *a*, but the obstacle has so far been one of obtaining suitable crystals. At Mellon Institute an investigation has been begun into the feasibility of growing crystals of mater-

ials which are similar to chlorophyll in the belief that successful X-ray analyses of such compounds could perhaps contribute to a better understanding of their chemical and physical properties. To this end, three different compounds of deoxophylloerythroetioporphyrin (DPEP) were prepared and isolated by Earl W. Baker of this laboratory. Two were the Ni^{2+} and VO^{2+} metal chelates, and the third was the free base (hydrogen atoms on two of the four pyrrole nitrogen atoms). The DPEP was prepared by a method described elsewhere (Baker, Corwin, Klesper & Wei, 1968) using pheophytin (chlorophyll a with the Mg atom removed) as the starting material. The structural formulas for chlorophyll a and VO-DPEP are given in Fig. 1 for comparison. Although VO-DPEP has the same carbon–nitrogen skeleton as chlorophyll a, important differences are: the saturation state of the outer C–C bond of the pyrrole ring D; the different substituent atoms on the isocyclic ring E; the presence of a vinyl group in chlorophyll a as opposed to an ethyl group in VO-DPEP on the pyrrole ring A; and different metal chelating atoms. The unique feature of the VO-DPEP structure as compared with other porphyrin structures determined from X-ray analyses is the addition of the fifth isocyclic ring, E. This work was undertaken to measure the effect of the ring E on the porphyrin skeleton.

Experimental

Crystals suitable for an X-ray structure analysis were grown by vapor-phase diffusion of methanol into a 1,2-dichloroethane solution of VO-DPEP (Donnay & Storm, 1967). The VO-DPEP solution was put into a 50 ml beaker which in turn was placed in a small desiccator containing methanol. The VO-DPEP is insoluble in methanol, and after two weeks in the sealed desiccator enough methanol diffused into the solution to cause the formation of beautiful crystals of VO-DPEP. The crystals are deep red, flat diamond-shaped plates 0·10–0·16 mm on an edge and 0·05 mm thick. A crystal was mounted on a small glass fiber with a drop of glyptal and aligned visually along the body diagonal, which corresponds to the b crystallographic axis. Preliminary Weissenberg photographs indicated that the space group was probably $P2_1/a$. Accurate cell dimensions were determined from precise diffractometric measurements of the 2θ values of the more intense higher-angle reflections. The cell dimensions were refined with a least-squares computer program on the

basis of 2θ values for 20 reflections. The density was measured experimentally by flotation in a potassium iodide solution. Pertinent crystal data are given in Table 1. Note that there is a 1:1 molecular ratio of solvent to VO-DPEP, as ascertained from the density measurement.

Data were collected by the θ–2θ scan technique (Alexander & Smith, 1962) with a General Electric
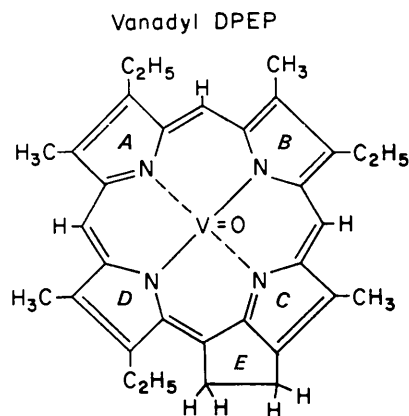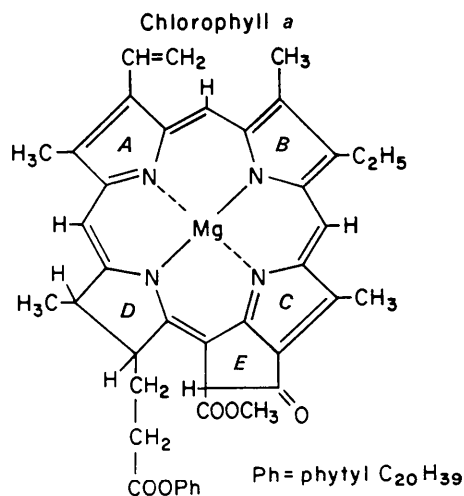

Fig. 1. A comparison of the structural formulas for chlorophyll a and VO-DPEP. Important differences are: the saturation state of the outer C–C bond of the pyrrole ring D; the different substituent atoms on the isocyclic ring E; the presence of a vinyl or ethyl group on ring A; and the different metal chelate atom in the center of the molecule.

Table 1. *Crystallographic data for* VO-DPEP *ethylene dichloride solvate*

Monoclinic, $P2_1/a$	$Z=4$
$a = 17\cdot963\ (3)$ Å	Empirical formula, $C_{32}H_{34}N_4VO \cdot C_2H_4Cl_2$
$b = 13\cdot961\ (1)$	M.W. $= 640\cdot54$
$c = 14\cdot090\ (3)$	$D_m = 1\cdot35$ g.cm^{-3}
$\beta = 116\cdot97\ (1)^\circ$	$D_x = 1\cdot35$ g.cm^{-3}
$V = 3149\cdot3$ Å^3	$F(000) = 1340$

$\mu l = 0\cdot9$ for longest crystal dimension (Cu $K\alpha$ radiation).

automated diffractometer equipped with a NaI scintillation counter and pulse-height analyser. Intensity data were recorded on punched tape with background counts taken before and after each 2θ scan. A scan of $3°$ was used for each reflection. A total of 1911 independent reflections was measured to a 2θ limit of $80°$, or $(\sin\theta)/\lambda = 0·417$. Of these, 1358 were measured twice for $2\theta \le 60°$, making use of the equivalent pairs $hkl = h\bar{k}\bar{l}$ and $\bar{h}kl = hk\bar{l}$.

A data reduction program written by P. Isaacs & G. S. Smith and subsequently revised by R. F. Stewart was used to convert the measured integrated intensities to relative structure factors. This program also applies the Lorentz (L) and polarization (p) corrections and calculates the statistical variances of the relative structure factors, taking account of counting statistics and time-dependent instability of the apparatus and the crystal. A reflection was classed as unobserved when $I_o \le 1·5\sigma(I_o)$, yielding a total of 534 unobserved reflections. In the least-squares refinement of atomic parameters, the function minimized was $\Sigma w(F_o - F_c)^2$, where the weights w are defined by $w = 1/\sigma_{Fo}$.

For observed reflections

$$\sigma_{Fo} = \tfrac{1}{2}\sigma_{Io} . (\text{L} . \text{p} . I_o)^{-1/2}$$

and for unobserved reflections

$$\sigma_{Fo} = \tfrac{1}{2}F_o/1·5 = \tfrac{1}{3}F_o ,$$

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

$$F_o = [1/(\text{Lp}) . 1·5\sigma(I_o)]^{1/2} .$$

The pairs of F_o's from equivalent reflections were averaged and a new σ computed for the average by use of the relation (Paradine & Rivett, 1953)

$$\frac{1}{\sigma_{av}^2} = \frac{1}{\sigma_1^2} + \frac{1}{\sigma_2^2} .$$

No attempt was made to reclassify any of the unobserved reflections on the basis of the new σ's for the average of two equivalent reflections. No corrections were made for absorption or extinction because of the low absorption factor and the small size of the crystal.

The processed data were loaded onto magnetic tape by the program *Data Reduction* of the *X-ray* 63 *System* (Stewart & High, 1965). Scattering factors were taken for the neutral atoms from *International Tables for X-ray Crystallography* (1962). All computing except the final three cycles of least-squares refinement was done with the *X-ray* 63 *System Programs* on an IBM 7090 computer. The final cycles of least-squares refinement were done with anisotropic thermal parameters for the vanadium atom and the atoms of 1,2-dichloroethane. At this point the number of parameters (194) exceeded the limits for the IBM 7090 computer, and the remaining least-squares refinement was carried out on an IBM 360 computer.*

Structure determination

The structure was solved by the conventional heavy-atom method. Atomic coordinates for the vanadium atom were uniquely determined from a three-dimensional sharpened Patterson vector map. The positional parameters and an isotropic temperature factor of $B = 3·0$ Å^2 for this atom were used to calculate phases and structure factors for all the reflection data. Agreement between the observed and calculated structure factors gave a conventional R index of 53%, where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. A Fourier synthesis computed using these phases and the observed structure factors revealed positions for 20 atoms of a plausible structure, which included the oxygen atom of the vanadyl group, the four pyrrole nitrogen atoms, thirteen of the 20 carbon atoms in the porphyrin skeleton, and two atoms of the attached methyl or ethyl groups. Isotropic temperature factors of $B = 4·0$, $5·0$ and $6·0$ Å^2 were assigned respectively to the nitrogen, oxygen and carbon atoms, and a second electron density map was computed with the use of the phases calculated from the parameters of the above-mentioned atoms plus the vanadium atom. The R value remained at 53%, but much more of the structure was apparent. A likely structure for the entire porphyrin skeleton (20 carbon and 4 nitrogen atoms) was determined in addition to eight methyl and ethyl side-chain atoms. A third cycle of structure factors lowered R to 46%.

During this time, of course, an expectant watch was being made for the four atoms of 1,2-dichloroethane, the solvent molecule of crystallization. To this point the only evidence for its presence had been the density measurement. The Patterson map did not show any outstanding peaks that could be interpreted as denoting chlorine atom positions, and in retrospect it still does not. Two broad peaks which appeared to be isolated from the main structure were observed in the early Fourier syntheses. The heights of these two peaks were only slightly greater than the heights for those peaks assigned to carbon and nitrogen atoms. After the third Fourier synthesis it was decided to include parameters for the 1,2-dichloroethane atoms in the next cycle of structure factor and phase calculations. The coordinates of the two broad peaks were assigned to the chlorine atoms, and coordinates from a much lower elongated peak were chosen for the two carbon atoms. At this point all but four atoms of the structure were included, the four being three carbon atoms of the methyl and ethyl side groups and one carbon atom needed to complete the isocyclic ring E. The agreement

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* For this purpose a program *SFLS*-5 by Prewitt (1966) was employed.

between observed and calculated structure factors was 42% and the corresponding Fourier synthesis clearly revealed the remaining four carbon atoms.

The positional parameters for the complete structure along with isotropic temperature factors assigned to each atom were refined by two cycles of full-matrix least-squares. The weighted R dropped to 30·1% after the first cycle and to 20·7% after the second, indicating the structure to be essentially correct. The thermal parameters of all the atoms were reasonable ($B = 8·0$ Å^2 or less), except those for the atoms of 1,2-dichloroethane ($B = 11$ to 15 Å^2). A difference synthesis was calculated subtracting all of the refined structure except the 1,2-dichloroethane to see if there might be any evidence of disorder in that molecule. The two chlorine peaks appeared well resolved, but very broad. The peak heights were 5·1 and 4·0 e.Å^{-3} respectively. If 0·5 e.Å^{-3} is used as a lower limit, the longest dimension of both peaks is along the a axis, estimated to be about 3·6 Å for Cl(1) and 2·5 Å for Cl(2). The other

dimensions along the b and c axes are approximately 2·0 Å for both peaks. A smeared elongated maximum appeared at the positions of the two carbon atoms, the largest part of it peaking at 1·9 e.Å^{-3} and the other end peaking at 1·3 e.Å^{-3}. A disordered arrangement of the 1,2-dichloroethane atoms in the structure was ruled out because of the resolution of the two chlorine atom peaks and the presence of a single, although smeared peak for the two carbon atoms.

The least-squares refinement was continued with positional parameters for the 1,2-dichloroethane atoms determined from the peak locations of the difference synthesis. Initial isotropic thermal parameters for the solvent molecule atoms of $B = 10$ Å^2 were chosen. After four more cycles of least-squares, the weighted R was 9·8%. The B's of the 1,2-dichloroethane atoms returned to the values previously determined by the first two cycles of refinement.

Because of the high B values for the atoms of the solvent molecule, and because of the asymmetry of its

Table 2. *Fractional coordinates and thermal parameters for* VO-DPEP

Heavy atoms

	x	y	z	B
V	0·0880 (2)	0·1174 (2)	−0·0874 (2)	
Cl(1)	−0·0029 (5)	0·3017 (4)	0·4988 (6)	
Cl(2)	0·0648 (4)	0·0935 (4)	0·4813 (5)	
O	0·1295 (5)	0·1126 (7)	−0·1684 (6)	4·4 (2) Å^2
N(A)	−0·0210 (7)	0·1965 (8)	−0·1809 (9)	2·7 (3)
N(B)	0·1354 (6)	0·2405 (8)	0·0001 (8)	2·4 (3)
N(C)	0·1630 (7)	0·0488 (8)	0·0421 (9)	3·1 (3)
N(D)	0·0128 (6)	−0·0087 (8)	−0·1290 (8)	2·2 (3)
C(1)	−0·0921 (10)	0·1553 (12)	−0·2586 (13)	4·4 (4)
C(2)	−0·1441 (9)	0·2321 (12)	−0·3174 (12)	4·7 (4)
C(3)	−0·1064 (10)	0·3160 (11)	−0·2763 (12)	3·8 (4)
C(4)	−0·0258 (9)	0·2973 (11)	−0·1841 (12)	3·4 (4)
C(5)	0·0349 (9)	0·3570 (9)	−0·1153 (11)	2·7 (4)
C(6)	0·1068 (9)	0·3318 (10)	−0·0294 (11)	2·8 (4)
C(7)	0·1681 (9)	0·3971 (11)	0·0418 (12)	3·6 (4)
C(8)	0·2328 (9)	0·3500 (10)	0·1174 (12)	3·6 (4)
C(9)	0·2102 (9)	0·2474 (10)	0·0917 (11)	2·9 (4)
C(10)	0·2618 (8)	0·1713 (11)	0·1527 (11)	3·4 (4)
C(11)	0·2366 (9)	0·0743 (10)	0·1308 (11)	3·0 (4)
C(12)	0·2878 (8)	−0·0047 (11)	0·1938 (10)	2·7 (3)
C(13)	0·2393 (9)	−0·0798 (10)	0·1430 (11)	2·7 (4)
C(14)	0·1672 (9)	−0·0504 (11)	0·0536 (11)	2·6 (4)
C(15)	0·1071 (9)	−0·1168 (11)	−0·0089 (11)	2·9 (3)
C(16)	0·0335 (9)	−0·1027 (11)	−0·0971 (11)	3·0 (4)
C(17)	−0·0329 (9)	−0·1647 (10)	−0·1637 (11)	2·8 (4)
C(18)	−0·0940 (9)	−0·1145 (11)	−0·2411 (11)	3·2 (4)
C(19)	−0·0649 (9)	−0·0157 (11)	−0·2216 (11)	3·3 (4)
C(20)	−0·1100 (9)	0·0614 (12)	−0·2752 (11)	4·1 (4)
C(21)	−0·2280 (9)	0·2201 (11)	−0·4172 (12)	6·4 (5)
C(22)	−0·1393 (9)	0·4206 (11)	−0·3078 (12)	6·1 (5)
C(23)	−0·1242 (10)	0·4592 (11)	−0·3949 (12)	8·0 (5)
C(24)	0·1551 (9)	0·5095 (11)	0·0319 (11)	5·5 (4)
C(25)	0·3084 (8)	0·3865 (11)	0·2120 (11)	4·4 (4)
C(26)	0·3026 (9)	0·3876 (12)	0·3175 (11)	7·0 (5)
C(27)	0·3686 (9)	0·0035 (10)	0·2964 (12)	6·0 (4)
C(28)	0·2388 (8)	−0·1913 (10)	0·1447 (11)	3·6 (4)
C(29)	0·1509 (9)	−0·2131 (10)	0·0470 (12)	5·2 (4)
C(30)	−0·0323 (8)	−0·2762 (11)	−0·1499 (11)	5·3 (4)
C(31)	0·0016 (9)	−0·3268 (11)	−0·2208 (12)	7·0 (5)
C(32)	−0·1753 (8)	−0·1466 (9)	−0·3316 (10)	3·6 (4)
C(33)	0·0301 (18)	0·2127 (18)	0·5986 (20)	
C(34)	0·0542 (22)	0·1265 (17)	0·5964 (21)	

Table 2 (cont.)

Anisotropic B_{ij}'s*

	B_{iso}†	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	3·5 Å²	3·5 (2)	3·2 (1)	4·4 (2)	0·3 (2)	2·2 (1)	0·3 (2)
Cl(1)	16·3	26·1 (7)	11·9 (5)	12·2 (5)	4·9 (5)	9·9 (5)	1·2 (4)
Cl(2)	12·4	16·2 (5)	11·4 (5)	15·0 (5)	−1·4 (4)	11·8 (4)	−0·7 (4)
C(33)	13·3	18·5 (2·1)	14·5 (2·3)	9·5 (1·8)	9·3 (2·2)	8·8 (1·6)	10·5 (2·1)
C(34)	15·4	32·6 (3·5)	9·0 (2·0)	9·4 (1·9)	−1·8 (2·3)	13·6 (2·3)	−2·9 (1·9)

* The anisotropic thermal parameters were introduced in the form $\exp[-(\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{12}hk-2\beta_{13}hl-2\beta_{23}kl)]$, $B_{11}=4\beta_{11}/a^{*2}$, etc.

† The equivalent isotropic temperature factor.

Hydrogen atoms

	x	y	z	B
H(5)	0·039	0·441	−0·096	5·0 Å²
H(10)	0·328	0·202	0·266	5·0
H(20)	−0·167	0·024	−0·353	5·0
H(21A)	−0·260	0·152	−0·420	8·0
H(21B)	−0·237	0·286	−0·402	8·0
H(21C)	−0·226	0·234	−0·483	8·0
H(22A)	−0·198	0·444	−0·328	8·0
H(22B)	−0·114	0·475	−0·245	8·0
H(23A)	−0·150	0·499	−0·445	8·0
H(23B)	−0·134	0·418	−0·462	8·0
H(23C)	−0·070	0·472	−0·376	8·0
H(24A)	0·199	0·515	0·101	7·0
H(24B)	0·141	0·504	−0·032	7·0
H(25A)	0·362	0·420	0·251	8·0
H(25B)	0·397	0·334	0·284	8·0
H(26A)	0·291	0·314	0·346	8·0
H(26B)	0·255	0·417	0·302	8·0
H(27A)	0·398	−0·035	0·275	8·0
H(27B)	0·361	−0·022	0·362	8·0
H(27C)	0·383	0·039	0·374	8·0
H(28A)	0·299	−0·220	0·154	5·0
H(28B)	0·256	−0·218	0·232	5·0
H(29A)	0·176	−0·244	0·021	5·0
H(29B)	0·094	−0·243	0·039	5·0
H(30A)	−0·012	−0·285	−0·103	6·0
H(30B)	−0·122	−0·258	−0·252	6·0
H(31A)	−0·025	−0·285	−0·305	9·0
H(31B)	0·050	−0·307	−0·211	9·0

peaks from the difference Fourier synthesis, it was decided to refine this portion of the structure with anisotropic thermal parameters. Vanadium was also assigned anisotropic temperature parameters. The rather limited number of reflections (~ 2000) prohibited refinement of additional atoms anisotropically. (Including the unobserved reflections, the ratio of the number of data to parameters was exactly ten.) The vanadium and chlorine atoms were corrected for both the real and imaginary components of anomalous dispersion in the final structure factor calculations (Dauben & Templeton, 1955). The values used for vanadium were $\Delta f' = 0\cdot1$, $\Delta f'' = 2\cdot3$, and for chlorine $\Delta f' = 0\cdot3$, $\Delta f'' = 0\cdot7$ for all reflections. After three cycles of refinement including both observed and unobserved reflections the unweighted R was 16·6% and the weighted R 8·4%. Two more cycles omitting the unobserved reflections gave an unweighted R of 12·3% and a weighted R of 8·3%. The last two cycles had little or no effect on the struc-

tural parameters and very small increases were observed for the estimated standard deviations.

An attempt was also made to refine the structure in the same manner as described above with the additional feature of varying the occupation factors for the atoms of 1,2-dichloroethane. The results were quite unsatisfactory, the factors varying from 0·94 to 0·92 for the two chlorine atoms and from 0·80 to 1·55 for the two carbon atoms after two cycles.

A difference synthesis was calculated using the refined structural parameters to determine if any of the hydrogen atoms could be located. The positions of 17 of the hydrogen atoms were first calculated by the heavy atom coordinates. The remaining 21 hydrogen atoms are attached to methyl groups and their positions could not be calculated. Fourteen of the seventeen hydrogen atoms showed up as reasonable peaks (0·3–0·5 e.Å⁻³) in the difference electron density map at or near their calculated positions. The four which

could not be located were those of the 1,2-dichloroethane molecule. In addition 15 of the 21 methyl hydrogen atoms appeared at reasonable positions and at heights of 0·3–0·5 e.Å^{-3}. At the suggestion of one of the referees and of the editor, these 28 locatable hydrogen atoms were included for additional structure factor and full-matrix least-squares refinement calculations. Isotropic *B*'s of 5·0, 6·0, 7·0, 8·0, or 9·0 Å^2

Table 3. *The observed and calculated structure factors for* VO-DPEP

H	L	FOBS	FCAL
**K =		0****	
0	1	201	226
0	2	36	42
0	3	103	109
0	4	11	3
0	5	72	72
0	6	33	33
0	7	13	13
0	8	12	8
0	9	19	11
0	10	28	21
2	-11	29	20
2	-10	48	51
2	-9	40	39
2	-8	69	73
2	-7	10	5
2	-6	9	1
2	-5	42	40
2	-4	107	106
2	-3	217	211
2	-2	36	35
2	-1	16	13
2	0	104	101
2	1	156	157
2	2	109	110
2	3	63	64
2	4	17	23
2	5	77	74
2	6	28	30
2	7	69	63
2	8	20	21
2	9	46	39
4	-11	32	38
4	-10	21	24
4	-9	38	34
4	-8	40	43
4	-7	54	51
4	-6	46	43
4	-5	51	45
4	-4	390	382
4	-3	627	612
4	-2	98	100
4	-1	41	40
4	0	16	22
4	1	55	58
4	2	24	30
4	3	35	39
4	4	22	15
4	5	23	24
4	6	30	25
4	7	12	6
4	8	14	5
6	-11	58	56
6	-10	39	36
6	-9	11	3
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2	-4	12	14
2	-3	27	32
2	-2	11	6
2	-1	34	31
2	0	29	36
2	1	20	22
2	2	14	16
2	3	21	21
2	4	30	27
2	5	16	8
3	-7	12	4
3	-6	17	25
3	-5	18	20
3	-4	19	19
3	-3	40	40
3	-2	38	34
3	-1	24	13
3	0	11	4
3	1	30	32
3	2	54	52
3	3	49	52
3	4	28	20
3	5	13	2
4	-7	13	7
4	-6	16	19
4	-5	24	20
4	-4	12	7
4	-3	21	25
4	-2	36	38
4	-1	12	3
4	0	12	6
4	1	28	30
4	2	12	14
4	3	12	9
4	4	15	15
5	-7	36	42
5	-6	31	31
5	-5	26	30
5	-4	12	6
5	-3	19	16
5	-2	48	49
5	-1	62	62
5	0	46	48
5	1	32	27
5	2	17	15
5	3	12	6
6	-7	13	14
6	-6	13	3
6	-5	12	5
6	-4	27	29
6	-3	26	30
6	-2	12	13
6	-1	12	4
6	0	20	17
6	1	19	16
6	2	12	8
6	3	13	10
7	-6	20	20
7	-5	34	29
7	-4	15	7
7	-3	12	4
7	-2	18	13
7	-1	22	20
7	0	28	23
7	1	12	5
8	-6	31	36
8	-5	18	19
8	-4	14	12
8	-3	12	9
8	-2	13	16
8	-1	13	14
8	0	13	2
9	-5	35	35
9	-4	40	40
9	-3	32	29
9	-2	17	13
**K =		10****	
0	0	43	48
0	1	12	1
0	2	12	8
0	3	43	47
0	4	12	1
0	5	13	3
1	-5	13	4
1	-4	19	19
1	-3	36	35
1	-2	29	25
1	-1	29	29
1	0	12	8
1	1	12	8
1	2	12	3
1	3	33	33
1	4	25	23
2	-5	26	18
2	-4	21	26
2	-3	30	28
2	-2	12	7
2	-1	22	20
2	0	33	36
2	1	31	33
2	2	30	28
2	3	12	1
2	4	17	11
3	-5	13	8
3	-4	18	18
3	-3	12	6
3	-2	12	2
3	-1	22	15
3	0	44	44
3	1	30	28
3	2	12	9
3	3	12	1
4	-5	13	14
4	-4	12	1
4	-3	19	20
4	-2	13	4
4	-1	12	10
4	0	16	17
4	1	17	23
4	2	12	2
4	3	13	7
5	-5	18	14
5	-4	16	16
5	-3	13	13
5	-2	37	35
5	-1	25	29
5	0	12	2
5	1	18	16
5	2	20	25
6	-5	13	5
6	-4	13	10
6	-3	13	19
6	-2	18	15
6	-1	13	5
6	0	13	7
6	1	14	9
7	-4	13	4
7	-3	20	21
7	-2	13	9
7	-1	19	20
**K =		11****	
0	1	16	17
0	2	41	40
0	3	42	42
1	-3	34	36
1	-2	14	11
1	-1	13	1
1	0	14	11
1	1	14	9
1	2	21	23
2	-3	18	22
2	-2	15	20
2	-1	13	5
2	0	22	14
2	1	13	4
2	2	13	13
3	-3	17	21
3	-2	13	6
3	-1	29	19
3	0	52	53
3	1	41	42
4	-3	20	16
4	-2	13	8
4	-1	23	21
4	0	33	28

were fixed for each hydrogen atom so as to be about 1 Å^2 greater than the *B* of the bonded carbon atom. The hydrogen parameters were held fixed and the heavy atoms were allowed to refine for one cycle of least-squares refinement. There was a noticeable shift in parameters, especially those of the alkyl side chains where some shifted as much as 2–3 times the computed error. This calculation was followed by a series of three

cycles of least-squares where the hydrogen atom co-ordinates were allowed to refine, and the remaining parameters were held fixed. Four more cycles were computed allowing the heavy atoms to refine and the hydrogen atoms were held fixed. The results of the last cycle gave a weighted R of 5·8%, and the computed standard errors had all dropped by 0·01 Å for bond

lengths and about 1·0° for bond angles. There also appeared to be a very slight 'shrinkage' of the entire porphyrin molecule as many of the bonds were short-ened by 0·01–0·02 Å.*

Although the refinement process had converged to a minimum, bond distances for two of the ethyl group side chains were unusually short [C(22)–C(23) = 1·43
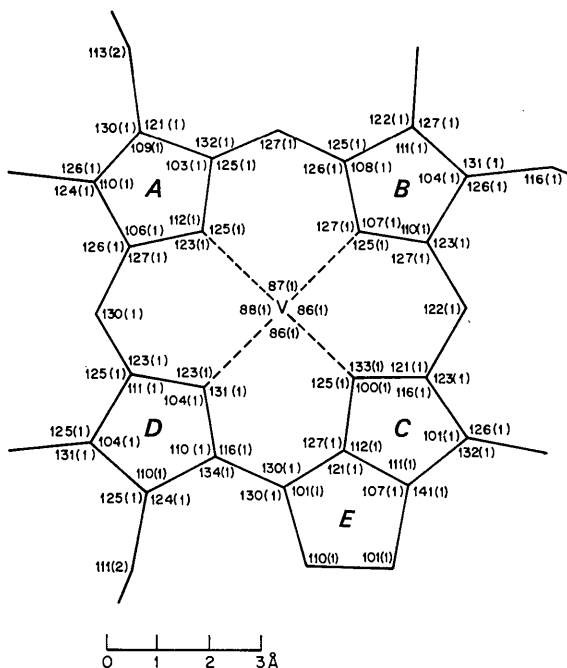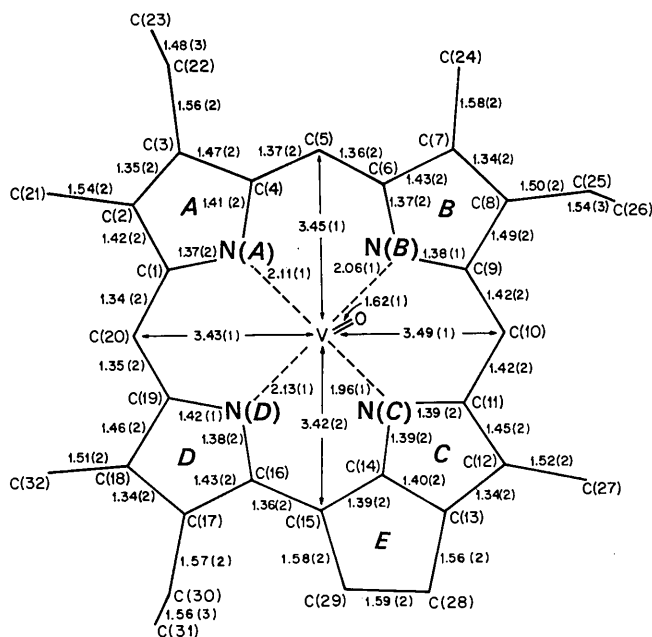
Fig. 2. Interatomic distances and angles for the VO-DPEP molecule from the fractional atomic coordinates listed in Table 2. The least-squares estimated standard deviations are given in parentheses.

and C(25)–C(26) = 1·48 Å]. To attempt a refinement to more reasonable bond lengths for the two ethyl side chains, it was decided to refine all of the side chain carbon atoms along with the coordinates for their hydrogen atoms which had been located and refined previously. The two carbon atoms of the isocyclic E ring, C(28) and C(29), plus their four hydrogen atoms were also allowed to refine. The remainder of the structure was held fixed and used only for the structure factor calculations. After two cycles, the bond distances of the two ethyl groups had improved to the more reasonable values of 1·47 Å for C(22)–C(23) and 1·53 Å for C(25)–C(26). Finally all of the heavy atom parameters were allowed to refine and the hydrogen atoms were held fixed. After two more cycles, the weighted R was 5·5% and the unweighted R was 14·0%, both of which included the unobserved reflections. The average shift per error at the end of the last cycle was 0·033. The structural parameters from the final calculation are listed in Table 2. The estimated standard deviations are given in parentheses for the heavy atoms and apply to the last significant figure. The Table also includes the parameters for the hydrogen atoms whose coordinates had been previously refined. Table 3 lists the observed and calculated structure factors for all the reflections. A difference map was computed subtracting all of the heavy atoms plus the 28 hydrogen atoms, but none of the remaining hydrogen atoms were evident.

Discussion of the structure

Fig. 2 shows a two-dimensional projection of the molecule and indicates the pertinent interatomic distances and angles. The least-squares estimated standard deviations are given in parentheses. Table 4 is a list of the C–H bond distances, but they should not be considered as accurate in relation to the heavy atom portion of the structure. Although the accuracy of the structure is low, the results indicate that there is a distortion in the fourfold symmetry normally found in porphyrin and porphine structures (Hoard, Hamor, Hamor & Caughey, 1965; Koenig, 1965; Fleischer, 1963; Webb & Fleischer, 1965). The distortion is presumably due to the introduction of the isocyclic ring E, which distinguishes this structure from the other porphyrin and porphine structures studied to date.

To evaluate the extent of the distortion, Cruickshank's criterion is applied to ascertain whether or not a measurement A is significantly different from a measurement B (Cruickshank, 1949). At a 99·9% confidence level the criterion states that the difference between two measurements A and B must be 3σ, where $\sigma = (\sigma_A^2 + \sigma_B^2)^{1/2}$. It is also recognized that the formally calculated standard deviations from the least-squares refinement are at best a minimum, and should be con-

A C 25B – 8

Table 4. *Carbon–hydrogen bond distances*

Standard errors are considered to be at least 0·1 Å.

C(5)—H(5)	1·2 Å		C(25)–H(25B)	1·6 Å
C(10)–H(10)	1·6		C(26)–H(26A)	1·2
C(20)–H(20)	1·2		C(26)–H(26B)	0·9
C(21)–H(21A)	1·1		C(27)–H(27A)	0·9
C(21)–H(21B)	1·0		C(27)–H(27B)	1·1
C(21)–H(21C)	1·0		C(27)–H(27C)	1·1
C(22)–H(22A)	1·0		C(28)–H(28A)	1·1
C(22)–H(22B)	1·1		C(28)–H(28B)	1·2
C(23)–H(23A)	0·9		C(29)–H(29A)	0·8
C(23)–H(23B)	1·1		C(29)–H(29B)	1·1
C(23)–H(23C)	0·9		C(30)–H(30A)	0·6
C(24)–H(24A)	0·9		C(30)–H(30B)	1·6
C(24)–H(24B)	0·8		C(31)–H(31A)	1·2
C(25)–H(25A)	1·0		C(31)–H(31B)	0·9

sidered to be somewhat larger than those printed in this paper. For this reason an additional factor of two has been applied to Cruickshank's criterion (*i.e.* a difference of 6σ) before accepting two measurements as being significantly different from one another. From Fig. 2 it is seen that the distortion is mainly in the region of the pyrrole ring C, which is to be expected since it is adjacent to the perturbing ring E. The pyrrole angles within the C ring at C(12) and C(13) are significantly different from one another by 7σ. If the angles of ring C are compared with the angles of the other three pyrrole rings, there is at least one pair of corresponding angles in each comparison that differ from one another by more than 7σ [*e.g.* C(12) with C(17); N(C) with N(A); and C(11) with C(1)]. The V–N(C) distance of 1·96 Å also satisfies the above criterion of being significantly shorter than the other three V–N distances, indicating that the E ring has the effect of displacing the C ring in the direction of the center of the molecule. The other three V–N distances agree well with the expected value of 2·11 Å for a vanadyl porphyrin (Zerner & Gouterman, 1966).

The bond angles of the isocyclic ring E range from 101° to 121°, clearly indicating an asymmetric and strained ring. Unexpected for the E ring are its relative planarity and coplanarity with the rest of the porphyrin skeleton. This means that the hydrogen atoms attached to C(28) and C(29) should be in an eclipsed conformation, introducing additional strain into this ring. All four hydrogen atoms of the E ring were easily located on the difference map described previously. Their coordinates were refined and the results indicate that the steric strain may be somewhat relieved by distorted bonding angles, the H–C–H angle at C(28) being 89° and that at C(29), 116°. Again it is recognized that the accuracy is low, but the discrepancy is large enough to conclude that the difference in the two angles is probably real.

The equation of the best least-squares plane fitted to all the atoms except the vanadyl group and the alkyl side chain groups is $14·57x - 0·57y - 12·51z = 1·765$. The displacements in ångströms of each atom from this plane are given in Table 5. The molecule is re-

markably planar, but appears to have the shape of a very shallow saucer with the peripheral carbon atoms of the pyrrole rings displaced in the positive direction and the inner atoms dipping in the negative direction as the distance from the molecular center decreases. Table 6 lists the dihedral angles between the planes of the four pyrrole rings, the four nitrogen atoms and the porphyrin skeleton. All are relatively coplanar with one another with the possible exception of the *D* ring in relation to rings *A* and *B*. As will be shown later in Fig. 5 of the crystal packing section, the *D* ring overlaps the V–N(*C*) bond of a symmetry-related porphyrin molecule 3·53 Å away. It might be conjectured at this point that the tilting of the *D* ring is the result of the overlap with the adjacent molecule.

Table 5. *Displacements from the best least-squares plane calculated with the use of all the atoms except V, O, and the methyl and ethyl side groups*

The equation of the plane is $14{\cdot}57X - 0{\cdot}57Y - 12{\cdot}51Z = 1{\cdot}765$.

	Displacement		Displacement
V	−0·54 Å	C(14)	−0·03 Å
O	−2·16	C(15)	+0·03
N(*A*)	−0·08	C(16)	+0·00
N(*B*)	−0·07	C(17)	+0·10
N(*C*)	−0·05	C(18)	+0·05
N(*D*)	−0·04	C(19)	−0·07
C(1)	−0·04	C(20)	−0·04
C(2)	+0·03	C(21)	−0·01
C(3)	+0·04	C(22)	+0·18
C(4)	+0·01	C(23)	−1·10
C(5)	+0·02	C(24)	+0·20
C(6)	+0·03	C(25)	+0·15
C(7)	+0·07	C(26)	+1·55
C(8)	+0·04	C(27)	+0·11
C(9)	−0·01	C(28)	−0·01
C(10)	−0·04	C(29)	+0·03
C(11)	+0·00	C(30)	+0·20
C(12)	−0·00	C(31)	−1·21
C(13)	+0·02	C(32)	+0·09

Table 6. *The dihedral angles between the best least-squares-planes of atoms in the various rings of* VO-DPEP

	A	B	C	D	E	N
A	–					
B	2·5	–				
C	4·3	3·7	–			
D	6·5	7·0	3·6	–		
E	3·1	3·6	1·7	3·5	–	
N*	3·4	3·5	1·1	3·5	0·6	–
P*	2·9	3·0	1·4	4·0	0·7	0·6

* N and P refer respectively to the best least-squares planes containing the four nitrogen atoms and the porphyrin skeleton, as described in the text.

Fig. 3 shows the geometrical details of the central part of the molecule. The four nitrogen atoms are planar within their standard deviations, and the vanadium atom lies 0·48 Å out of this plane. This value is in fair agreement with the value 0·5–0·8 Å predicted by molecular orbital calculations for a vanadyl porphyrin (Zerner & Gouterman, 1966). Experimentally it also compares with 0·475 Å for the iron atom of α-chlorohemin (Koenig, 1965) and 0·455 Å for the iron atom of methoxyiron(III) mesoporphyrin-IX dimethyl ester (Hoard, Hamor, Hamor & Coughey, 1965). The four nitrogen atoms do not form a perfect square, the N(*C*) atom being displaced in the direction of the vanadium atom. The center point of the plane shown in Fig. 3 is the geometric center of the four nitrogen atoms, but because the V–N(*C*) distance is shorter than the other three vanadium–nitrogen distances, it does not coincide with the point of perpendicular projection of the vanadium atom onto the plane. The angle which the vanadium atom subtends between these two points is 3° and the difference is too small to be visible in the Figure. The distances from the vanadium atom to the two different points on the plane are equal, to three significant Figures.
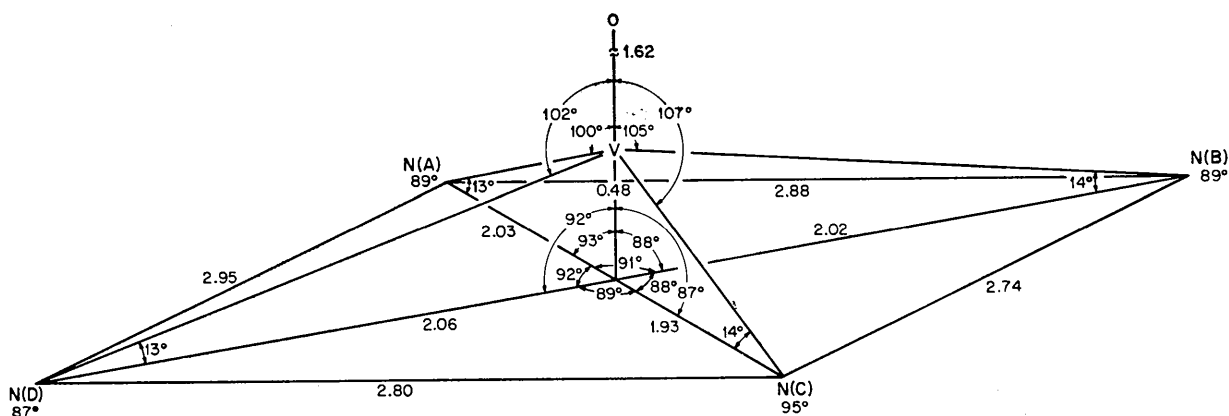

Fig. 3. The detailed geometry of the central part of the VO-DPEP molecule. The distances are given in Å and the angles in degrees. The center of the plane of the four nitrogen atoms is their geometric center. This point does not coincide with the point of perpendicular projection of the vanadium atom onto the nitrogen plane, but is displaced by a very small amount toward the N(*C*) atom. The V atom subtends an angle of 3° with these two points and the difference is too small to indicate in the Figure.

Fig. 3 also indicates a slight tilting of the vanadyl oxygen atom in the direction of the bridge carbon atom [C(20)] between the A and D pyrrole rings. The angles between the vanadium–oxygen vector and the four vanadium–nitrogen vectors are 100°, 104°, 107° and 102° respectively for the nitrogens of rings A, B, C and D. The V = O vector also intersects an angle of 3·2° with the vector normal to the best least-squares plane containing the four nitrogen atoms. This tilting of the oxygen atom appears to be due to some very weak hydrogen bonding with the solvent molecule of crystallization. Fig. 4, which will be introduced later in the discussion of crystal packing, shows the inter-atomic distances between the oxygen atom and the carbon atoms of 1,2-dichloroethane to be 3·26 and 2·96 Å, respectively, for C(33) and C(34).

The coordination geometry of the vanadium atom in this structure can be compared with that found in X-ray structures of other vanadyl complexes. As far as the author is aware, this is the first vanadyl structure determination for which the vanadium atom is coordinated with four nitrogen ligands. The others have oxygen atoms or at most one nitrogen atom as the coordinating ligands. The number of vanadyl struc-

tures published is becoming larger, and varying coordination geometry is reported. For example, the structure of tetrasodium divanadyl(IV) D-tartrate L-tartrate dodecahydrate, $Na_4(VO-DL-C_4H_2O_6)_2 \cdot 12H_2O$ (Tapscott, Belford & Paul, 1968), has a normal square-pyramidal configuration for the vanadium atom, similar to VO-DPEP. In the tartrate case the vanadium atom lies 0·546 Å above the best plane of the four coordinating tartrate oxygen atoms. The V = O bond distance in this structure is 1·619 (7) Å. The corresponding figures for VO-DPEP are 0·48 and 1·62 Å. Applying ligand-field theory, one would expect the vanadium atom to be drawn closer into the plane of the coordinating ligands for the VO-DPEP case because of the increased ligand-field strength of nitrogen as compared with oxygen. One might also expect the vanadyl bond to lengthen for VO-DPEP because of the repulsion of the oxygen atom by the π electrons of the porphyrin skeleton as the vanadium atom is drawn closer to the plane of the four nitrogen atoms.

A second example of a vanadyl complex is ammonium vanadyl (+)-tartrate monohydrate, $(NH_4)_2VO(C_4H_2O_6) \cdot H_2O$ (Forrest & Prout, 1967). The coordination geometry of the vanadium atom in
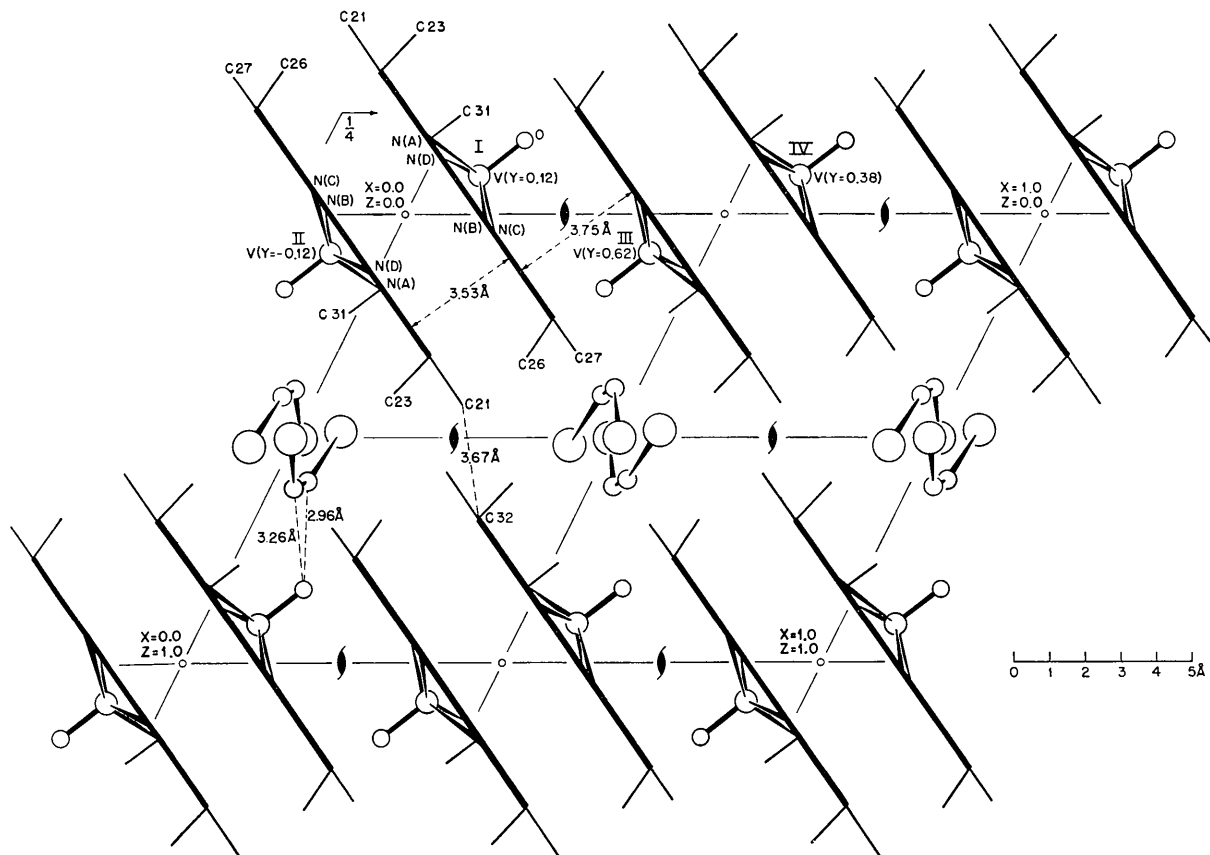

Fig. 4. The crystal packing as viewed in a projection along **b**. The solid bar represents the best least-squares plane of the porphyrin skeleton, its width being determined such that the area of the bar includes all the points of projection for each atom in the porphyrin skeleton plus the side chain atoms C(22), C(24), C(25), C(30) and C(32). The other atoms outside of this area are indicated in the drawing. The large rectangle represents one unit-cell.

this compound is a distorted trigonal bipyramid with the vanadyl oxygen in the equatorial plane of the bipyramid. The vanadyl bond length is 1·60 (2) Å. A third example is the structure of vanadyl sulphate pentahydrate, $VO(H_2O)_4(SO_4).H_2O$ (Ballhausen, Dju-

rinsky & Watson, 1968). The vanadium atom in the structure is surrounded by a distorted octahedron of six oxygen atoms. The coordinating oxygen of the sulphate group is *cis* to the vanadyl oxygen and the V=O bond length is 1·591 (5) Å. The vanadium atom

Table 7. *Intermolecular distances less than* 3·70 Å

Roman numerals refer to molecules shown in Figs. 4 and 5.

Molecule I to molecule II

N(A)–C(29)	3·61 Å
N(B)–C(17)	3·70
N(B)–C(30)	3·42
N(C)–C(18)	3·66
C(1)—C(28)	3·69
C(1)—C(29)	3·68
C(2)—C(28)	3·59
C(6)—C(30)	3·44
C(9)—C(30)	3·66
C(10)–C(32)	3·53
C(11)–C(18)	3·59
C(11)–C(32)	3·61
C(13)–C(20)	3·59

Molecule I to molecule III

O——C(25)	3·49
O——C(28)	3·53
C(7)–C(13)	3·68

Molecule II to molecule related by a twofold screw axis at $x=\frac{1}{4}$, $z=\frac{1}{4}$

| C(21)–C(32) | 3·67 |

VO-DPEP – Ethylene dichloride

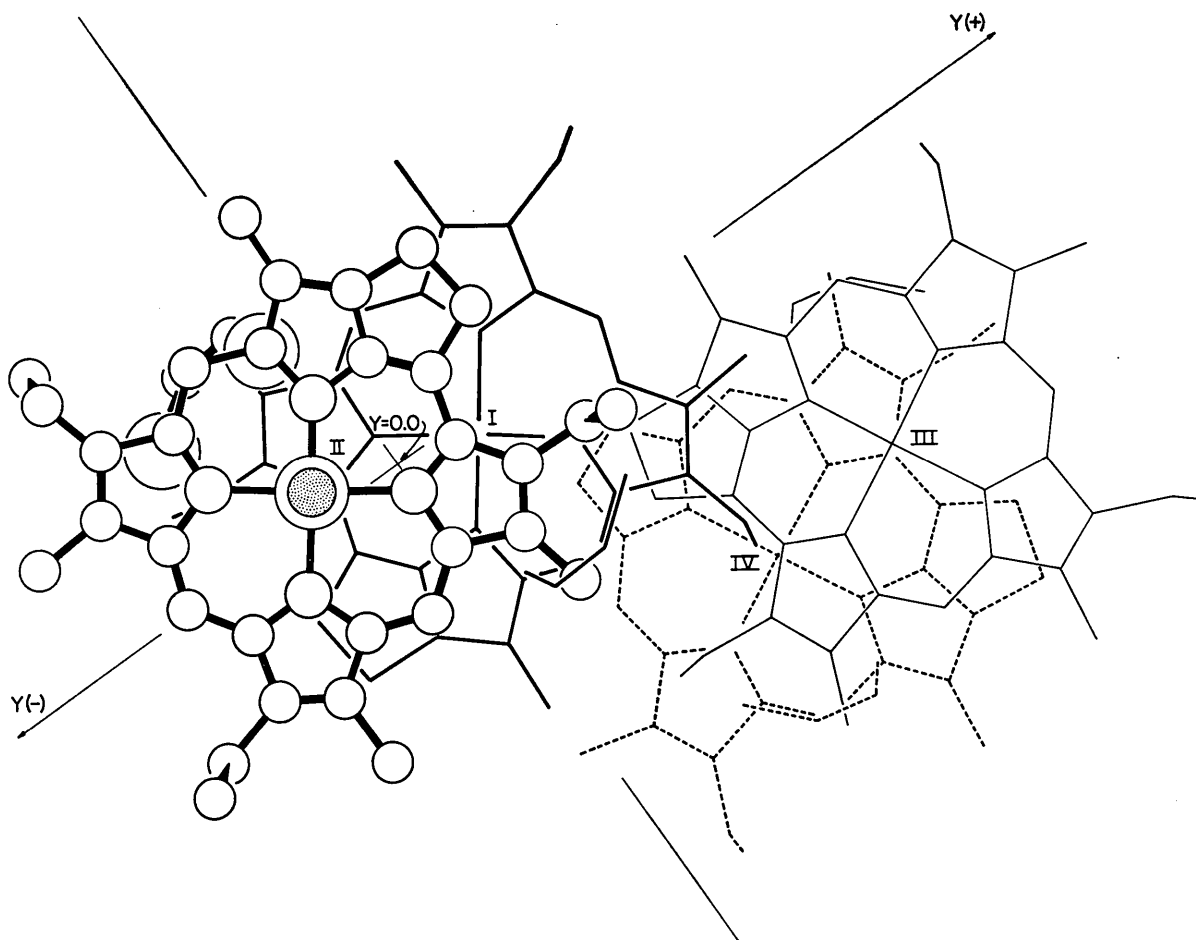| O——C(33) | 3·26 |
O——C(34)	2·96
N(A)–C(33)	3·62
C(1)—C(33)	3·68
C(18)–Cl(2)	3·66

Fig. 5. A projection of the unit-cell contents onto the plane of the four pyrrole nitrogen atoms. The projection of the Y direction is shown for reference. It intersects the plane of the page at $y=0·0$ and makes an angle of $-3°$ with the plane of the page for Y positive. The second axis is perpendicular to the Y projection and is a combination of the X and Z directions.

lies 0·281 Å out of the best plane of the four equatorial oxygen atoms. A much smaller out-of-plane distance would be expected of course, since there is a fifth co-ordinating oxygen ligand *trans* to the vanadyl oxygen atom.

Crystal packing

The VO-DPEP molecules pack parallel to one another and nearly parallel to the b axis, as seen from the equation for the best least-squares plane. The ethylene dichloride molecules fill up holes between the edges of the VO-DPEP molecules and stack in clusters of two molecules each along the b direction. Fig. 4 shows the crystal packing in a projection along the b axis. The solid bar is representative of the best least-squares plane of the porphyrin skeleton and its width was de-termined by the displacements of the atoms from the best plane such that the area of the bar included all the points of projection for each atom in the porphyrin skeleton plus the side chain atoms C(22), C(24), C(25), C(30) and C(32). The atoms outside this area are indi-cated in the Figure. There are two interplanar spacings between the best least-squares planes of the molecule: one of 3·53 Å between molecules related by a center of symmetry and where the vanadyl groups point away from one another; the second of 3·75 Å between mol-ecules related by a twofold screw axis and where the vanadyl groups point toward one another.

The solvent molecule of crystallization has been forced into its position with a *cis* configuration. From the refined positional parameters, the twist of the two chlorine atoms from one another about the C–C bond is only 6°. The Cl(1)–Cl(2) distance is 3·20 (1) Å, much shorter than the distance of 4·24 (2) Å found for the low-temperature form of 1,2-dichloroethane (Reed & Lipscomb, 1953). The two Cl–C distances are 1·77 (3) and 1·78 (4) Å and the C–C bond length is 1·28 (4) Å; the bond angles are 129 (3) and 116 (2)°. These values compare with 1·80 (2) Å for Cl–C; 1·49 (4) Å for C–C; and 105·5 (5)° for the angle in the low-temperature structure of 1,2-dichloroethane. Two 1,2-dichloro-ethane molecules are related by a center of symmetry and are quite tightly packed together. The Cl(2)–Cl(2) distance across the symmetry center is only 3·69 Å, and the corresponding Cl(2)–C(34) distance is 3·62 Å. There is no possibility of these two chlorine atoms being part of the same molecule as the symmetry center would not allow fitting in of the carbon atoms without a great distortion the molecule. Thus two molecules cluster tightly about the symmetry center and the shortest distance between the clusters is 5·52 Å from Cl(1) to Cl(1). [The Cl(1) atoms are those seen directly over the symmetry centers in Fig. 4.] This large space between the clusters is thought to be a contributing factor to the large thermal motion of the 1,2-dichloro-ethane.

Fig. 5 shows another projection of the unit-cell con-tents along the vector perpendicular to the plane of the four nitrogen atoms. The projection of the Y direc-tion is also shown for reference. It intersects the plane of the page at y=0·0 and makes an angle of −3° with the plane of the page for Y positive. The second axis in the Figure is perpendicular to the Y projection and is a combination of the X and Z directions. The Roman numerals for each molecule can be matched to those of Fig. 4 if the Y direction shown in the Figure is imagined to be perpendicular to the page of Fig. 4. Fig. 5 also shows that there is partial overlap of the molecules, most of it being between molecules I and II, which are related by a center of symmetry. Table 7 lists all the intermolecular distances less than 3·70 Å.

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