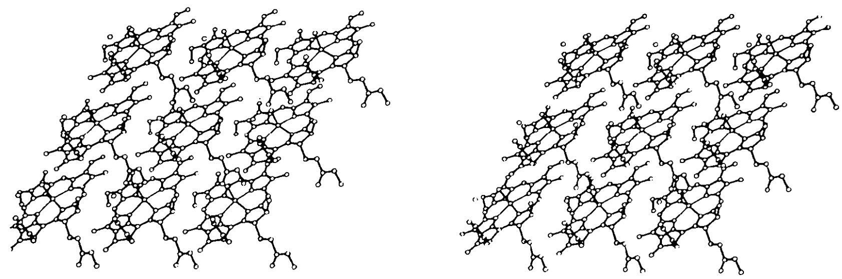

Fig. 2. Packing of methylchlorophyllide A molecules in a two-dimensional layer. The projection is down **b**; **a** runs right to left, and **c** (the propagation direction of the one-dimensional stacks) upwards at an angle turned 30° clockwise from the vertical direction.

The Mg atom is 0·34 Å from the mean plane of its four N ligands and is also coordinated to a fifth ligand [the water molecule O(6)] at 2·03 Å. This water molecule forms a hydrogen bond to the carbonyl O(1) of the molecule related by the 8·42 Å translation [O(6)···O(1)(*x*, *y*, *z* + 1), 2·72 Å], giving rise to one-dimensional stacks along **c**. The second water molecule O(7) is involved in three hydrogen bonds: to O(6) [O(7)···O(6), 2·69 Å], to the ether O(3) [O(7)···O(3), 3·05 Å] and to the propionic acid ester carbonyl O(4) of the molecule related by the [101] translation [O(7)···O(4)(*x* + 1, *y*, *z* + 1), 2·75 Å]. The two-dimensional layer structure formed by this pattern of hydrogen bonds (Fig. 2) is very similar to that found in crystals of ethylchlorophyllide A and B (Strouse, 1974; Chow, Serlin & Strouse, 1975; Kratky & Dunitz, 1975); indeed, apart from differences in conformation of the propionic acid ester side-chain on ring IV and the methoxycarbonyl group on ring V, the structures are almost isomorphous in two dimensions. However, contacts between molecules belonging to adjacent layers are different in the two structures. In the ethylchlorophyllide structure, adjacent layers are related by a 3_1 axis, whereas in this structure they are related by a 2_1 axis.

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Methylpyrochlorophyllide A Monohydrate Monoetherate

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Abstract. Orthorhombic, $P2_12_12_1$, $a = 23\cdot01\,(3)$, $b = 19\cdot08\,(3)$, $c = 8\cdot42\,(1)$ Å; $C_{34}H_{34}O_3N_4Mg.H_2O.(C_2H_5)_2O$, $M_r = 663\cdot12$; $Z = 4$, $D_m = 1\cdot17$, $D_x = 1\cdot19$ g cm^{-3}. The five-coordinated Mg atom has as its fifth ligand a water molecule which is involved in two hydrogen bonds: one to a molecule of ether of solvation, the other to the ring V carbonyl O atom of the chlorophyll related by the [001] or [00$\bar{1}$] translation. The ether molecule and the ethyl substituent on ring II are disordered in the crystal.

Introduction. Crystals were obtained by slow evaporation from ether. The NMR spectrum (of a crystal dissolved in $CDCl_3$/10% CD_3OD) revealed the presence of ether in the crystal. Microprobe-analysis results and the observed density were best explained in terms of the formula unit $C_{34}H_{34}O_3N_4Mg.H_2O.(C_2H_5)_2O$ ($Z = 4$). Cell constants were obtained from precession photographs and diffractometer measurements.

The diffracted intensity shows a rapid fall-off with increasing scattering angle, reflexions beyond $d^* = 1{\cdot}0$ Å^{-1} being unobservable. Intensities of 2000 reflexions in the range $\theta \le 20°$ were measured on an automated four-circle diffractometer (Hilger & Watts Y290) with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The data were processed to yield 1256 reflexions with intensity significantly above background. Absorption corrections were not applied [μ(Mo $K\alpha$) = $0{\cdot}986$ cm^{-1}].

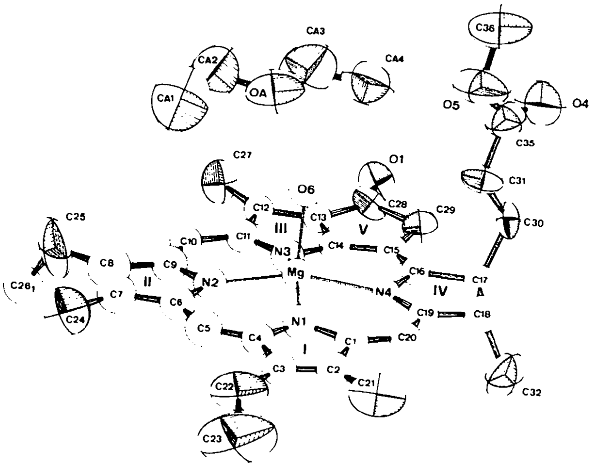

Fig. 1. Projection of the methylpyrochlorophyllide A molecule down **c**.

Table 1. *Fractional atomic coordinates* (×10⁴) *and vibrational tensor components* (×10⁴)

The temperature factors have the forms (*a*) for atoms refined isotropically $T = \exp[-(8\pi^2U_{\rm iso}\sin^2\theta/\lambda^2)]$; (*b*) for atoms refined anisotropically $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \cdots + 2hka^*b^*U_{12} + \cdots)]$. E.s.d.'s are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	5799 (5)	5321 (7)	−3996 (13)	777 (90)	902 (87)	382 (57)	−125 (81)	−30 (67)	227 (61)
O(4)	7423 (8)	6395 (9)	1950 (25)	1579 (159)	1154 (126)	2117 (198)	−180 (135)	971 (163)	−144 (156)
O(5)	6811 (8)	6554 (8)	3811 (22)	1973 (180)	780 (109)	1383 (139)	−74 (131)	590 (149)	−300 (107)
C(21)	5915 (13)	2729 (12)	8239 (24)	2131 (280)	971 (170)	530 (128)	56 (202)	43 (170)	−64 (131)
C(22)	4501 (13)	2675 (11)	8496 (23)	2331 (295)	840 (152)	539 (116)	58 (192)	490 (186)	525 (120)
C(23)	4510 (24)	2108 (16)	9120 (44)	4412 (647)	1419 (267)	2183 (376)	666 (359)	1974 (451)	1128 (263)
C(24)	2703 (12)	3527 (14)	4828 (36)	1312 (229)	1319 (225)	1960 (277)	−202 (224)	1205 (217)	459 (230)
C(25)	2542 (10)	4292 (16)	1294 (36)	646 (150)	2016 (282)	1669 (267)	− 386 (190)	153 (184)	638 (254)
C(27)	4183 (8)	5197 (11)	−3040 (20)	688 (133)	1122 (152)	440 (97)	−36 (131)	−212 (112)	132 (115)
C(28)	5735 (7)	5052 (8)	−2710 (16)	739 (124)	580 (108)	264 (72)	−219 (98)	−103 (93)	−23 (80)
C(29)	6262 (8)	4819 (9)	−1700 (21)	759 (127)	581 (110)	581 (109)	6 (111)	−32 (112)	145 (103)
C(30)	7160 (7)	4939 (9)	1601 (19)	316 (88)	805 (124)	526 (95)	−66 (99)	−81 (86)	−43 (108)
C(31)	6868 (9)	5423 (9)	2862 (21)	1063 (150)	515 (104)	472 (106)	−157 (118)	−175 (117)	−151 (93)
C(32)	7215 (11)	3063 (13)	2685 (31)	959 (174)	1296 (199)	1219 (206)	336 (157)	−171 (177)	481 (190)
C(35)	7072 (10)	6167 (10)	2821 (26)	1040 (172)	659 (128)	919 (142)	70 (124)	172 (149)	−171 (126)
C(36)	6971 (17)	7293 (14)	3802 (36)	2357 (349)	1098 (207)	1263 (223)	104 (250)	87 (278)	−411 (189)
O(*A*1)	4711 (8)	6344 (9)	1956 (20)	2036 (207)	1148 (116)	1265 (128)	78 (132)	−78 (137)	497 (117)
C(*A*1)	4074 (14)	6523 (18)	1752 (43)	1739 (286)	2013 (321)	2111 (360)	731 (296)	581 (296)	706 (332)
C(*A*2)	3746 (17)	6202 (24)	2897 (58)	1968 (349)	2423 (410)	2497 (421)	456 (325)	−101 (385)	−135 (408)
C(*A*3)	5035 (18)	6631 (17)	747 (37)	2068 (306)	1924 (275)	1871 (300)	539 (363)	647 (318)	1019 (254)
C(*A*4)	5646 (14)	6511 (14)	800 (43)	1635 (270)	962 (205)	2297 (340)	−324 (230)	−448 (278)	364 (247)

	x	y	z	$U_{\rm iso}$		x	y	z	$U_{\rm iso}$
Mg^{2+}	5027 (3)	4154 (3)	2854 (6)	515 (12)	C(9)	3723 (9)	4177 (11)	1647 (23)	755 (54)
N(1)	5092 (7)	3556 (7)	4877 (16)	683 (38)	C(10)	3877 (8)	4460 (9)	265 (21)	590 (50)
N(2)	4145 (6)	3973 (7)	2807 (17)	638 (41)	C(11)	4456 (8)	4575 (9)	−387 (20)	606 (51)
N(3)	4924 (7)	4365 (6)	453 (15)	611 (39)	C(12)	4607 (7)	4898 (8)	−1851 (18)	487 (42)
N(4)	5946 (6)	3983 (6)	2442 (14)	469 (34)	C(13)	5211 (6)	4842 (8)	−1889 (18)	458 (42)
O(6)	5073 (5)	5165 (5)	3580 (13)	629 (30)	C(14)	5405 (8)	4518 (9)	−403 (20)	591 (49)
C(1)	5616 (8)	3371 (9)	5545 (21)	630 (52)	C(15)	5991 (8)	4501 (9)	−180 (21)	547 (49)
C(2)	5458 (9)	3009 (9)	7134 (24)	754 (55)	C(16)	6243 (7)	4262 (9)	1181 (18)	483 (42)
C(3)	4896 (9)	2983 (8)	7219 (22)	712 (53)	C(17)	6900 (8)	4200 (9)	1461 (20)	591 (45)
C(4)	4663 (8)	3339 (9)	5796 (20)	647 (53)	C(18)	6942 (9)	3785 (10)	3015 (24)	794 (60)
C(5)	4105 (9)	3426 (11)	5517 (23)	762 (61)	C(19)	6337 (7)	3742 (9)	3558 (20)	569 (47)
C(6)	3818 (9)	3707 (11)	4160 (23)	756 (56)	C(20)	6170 (8)	3451 (9)	5011 (20)	580 (49)
C(7)	3202 (10)	3779 (12)	3714 (26)	908 (69)	C(26)1	2277 (30)	3856 (35)	313 (80)	1564 (255)
C(8)	3109 (10)	4092 (12)	2340 (29)	1033 (77)	C(26)2	2461 (34)	4957 (37)	1401 (80)	1622 (235)

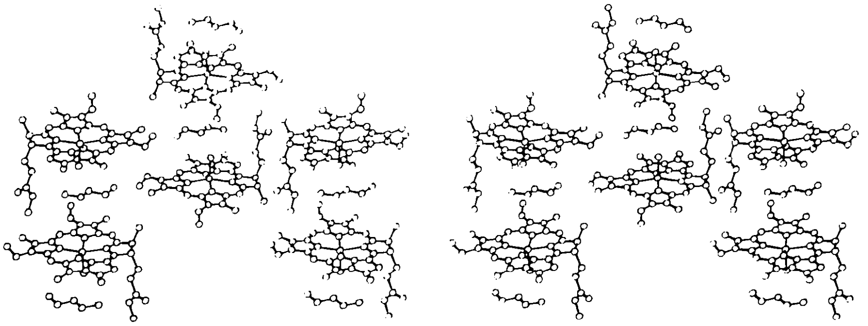

Fig. 2. Packing of methylpyrochlorophyllide A molecules. Stereo representation of the content of one unit cell, projected down **c**. The one-dimensional stacks mentioned in the text run perpendicular to the plane of the paper.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970). All 242 reflexions with $|E| \geq 1.5$ were included in the phase-determining process with 16 sets of starting phases. These led to only two significantly different E maps, in one of which 25 peaks could be recognized as forming a chemically reasonable pattern. The remaining atoms were identified from a series of F_o syntheses.

After seven cycles of full-matrix least-squares refinement (isotropic B's, $R = 0.13$), an $(F_o - F_c)$ synthesis indicated the positions of 31 H atoms, which were included in the structure factor calculations but not refined. Four more cycles of block-diagonal refinement with a modified weighting system (Dunitz & Seiler, 1973) with $w = [1/\sigma(F_o)] \exp[a(\sin\theta/\lambda)^2]$, $a = 10$ Å^2 and anisotropic temperature factors for 21 peripheral atoms (Fig. 1), yielded a final $R = 0.079$ for the 1032 reflexions with $|F_o| > 2.5\,\sigma(|F_o|)$.

Some atoms of the porphyrin substituents have fairly large and anisotropic vibrational ellipsoids, as indicated in Fig. 1. The methyl group C(26) of the ring II ethyl substituent was found to be distributed statistically between two positions, above and below the mean ring plane. It was included in the structure factor calculations at both positions with occupation factors of 0·5. The ether molecule is also affected by disorder, judging from the appearance of residual density peaks of up to 0·5 e Å^{-3} near the calculated positions of C(*A*1), C(*A*2), C(*A*3) and C(*A*4) in the final $(F_o - F_c)$ synthesis. Apart from these, no peaks higher than 0·3 e Å^{-3} were present.

The somewhat high R of 0·079 can be ascribed to two factors: inadequate description of the electron density in the disorder regions and the low average intensity of the reflexions. [Indeed, the expectation value of $R = \Sigma\sigma(|F_o|)/\Sigma|F_o|$ is 0·112.] Final positional and thermal parameters are given in Table 1.*

Discussion. The molecular structure is depicted in Fig. 1. Derived parameters (interatomic distances and angles, calculated H coordinates) are not listed here, but are recorded elsewhere (Kratky, 1976). Typical bond lengths and angles have e.s.d.'s of 0·01–0·02 Å and 1–2° respectively, and are reasonably consistent with the accepted chemical constitution, apart from a few exceptions which all involve atoms with unduly large, anisotropic temperature factors, *e.g.* atoms of the ether molecule and some of the porphyrin substituents, particularly C(22), C(23), C(24), C(25), C(27), C(28), C(29), O(1), O(4), O(5) and C(36), which have e.s.d.'s of up to 0·04 Å.

The Mg atom is displaced by 0·4 Å from the plane of its four N ligands and is also coordinated to a fifth ligand, the water molecule O(6), at 2·03 Å. The water molecule, in turn, is hydrogen bonded to a molecule of ether of crystallization [O(6)···O(*A*1), 2·76 Å] and to the carbonyl O of the pyrochlorophyllide molecule related by the **c** translation [O(6)···O(1), 2·65 Å]. This latter interaction leads to the formation of one-dimensional stacks of translationally equivalent molecules with an interplanar spacing of 3·41 Å (calculated for the mean plane of the inner ring atoms). Within a given stack, ring I of one molecule overlaps rings III and V of its translationally equivalent neighbour. Thus, the crystal consists of two sets of parallel stacks running along **c** and two sets of antiparallel stacks running along −**c**, all stacks being related either by translation or by the operation of the three sets of mutually orthogonal, non-intersecting screw axes (Fig. 2).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32134 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.