radius 3·3 Å, there are four other H atoms that belong to CH and CH$_3$ groups.

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Methylchlorophyllide A Dihydrate

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Abstract. Monoclinic, $P2_1$, $a = 8.76(1)$, $b = 25.86(3)$, $c = 8.47(1)$ Å, $\beta = 119.20(5)°$; $C_{36}H_{36}O_5N_4$·Mg·2H$_2$O, $M_r = 665.06$; $Z = 2$, $D_m = 1.30$; $D_x = 1.32$ g cm^{-3}. A net of hydrogen bonds gives rise to the formation of layers of chlorophyllide molecules, very similar to those found in crystals of ethylchlorophyllide A and B [Strouse, *Proc. Natl. Acad. Sci. US* (1974), **71**, 325–328; Chow, Serlin & Strouse, *J. Amer. Chem. Soc.* (1975), **97**, 7230–7237; Kratky & Dunitz, *Acta Cryst.* (1975), B31, 1586–1589].

Introduction. Crystals grown by slow evaporation from acetone/10% water under exclusion of oxygen were frequently twinned.* Intensities from a crystal fragment 0·5 × 0·3 × 0·05 mm were measured on an automated four-circle diffractometer (Hilger & Watts Y290) with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), yielding 2398 independent reflexions in the range $\theta \le 23°$. The data were processed to yield 1950 reflexions with intensity significantly above background [$|F_o| > \sigma(|F_o|)$]. No absorption correction was applied [$\mu(\text{Mo } K\alpha) = 1.158$ cm^{-1}].

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970). All 308 reflexions with $|E| > 1.4$ were included in the phase-determining process with 64 sets of starting phases. The E map calculated with phases from the solution with the best figures of merit contained 34 peaks forming a chemically reasonable pattern. After two cycles of least-squares refinement ($R = 0.29$), an F_o synthesis showed eight more atoms, which were included in four further cycles ($R = 0.19$). A second F_o synthesis then yielded the positions of the remaining six atoms.

After two cycles of full-matrix least-squares refinement with isotropic temperature factors for all atoms ($R = 0.11$), H atoms were included at calculated positions. The orientations of the terminal CH$_3$ groups were estimated from an ($F_o - F_c$) synthesis. Three cycles of block-diagonal least-squares refinement with anisotropic temperature factors for the peripheral atoms reduced R to 0·089, with H atom contributions included in F_c but not refined.

At this stage, scrutiny of the data revealed that the ($|F_o| - |F_c|$) values for reflexions measured at χ settings around 0° or 90° were systematically negative, suggesting that the corresponding intensities had been only partially recorded. The reflexions in question were remeasured with a larger collimator for the detector. Refinement was then continued with a separate scale factor for the set of 487 remeasured reflexions.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and vibrational tensor components* ($\times 10^4$)

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	920 (11)	1839 (3)	−7044 (10)	582 (47)	548 (47)	446 (40)	6 (40)	334 (37)	73 (38)
O(2)	−1420 (18)	2826 (5)	−5806 (22)	964 (87)	533 (67)	1673 (129)	210 (64)	529 (87)	311 (75)
O(3)	1132 (15)	2513 (4)	−3662 (12)	988 (75)	612 (54)	564 (50)	−84 (52)	421 (52)	−39 (43)
O(4)	−7368 (13)	2670 (4)	−8749 (11)	888 (65)	819 (65)	429 (42)	266 (57)	345 (45)	158 (45)
O(5)	−8024 (14)	3196 (4)	−7110 (12)	774 (61)	732 (64)	523 (49)	351 (53)	215 (45)	133 (45)
O(6)	1843 (11)	1195 (4)	1015 (11)	541 (47)	618 (53)	537 (46)	−5 (44)	293 (39)	35 (41)
O(7)	3308 (13)	1842 (5)	−345 (14)	742 (63)	842 (70)	805 (64)	45 (57)	440 (55)	36 (57)
C(21)	−4034 (15)	636 (5)	2669 (14)	555 (64)	554 (70)	442 (55)	−52 (61)	347 (52)	−17 (55)
C(22)	−1386 (17)	−343 (5)	4203 (16)	614 (77)	606 (82)	446 (64)	50 (66)	257 (61)	75 (59)
C(23)	−2318 (24)	−417 (8)	4934 (23)	972 (114)	1017 (126)	846 (107)	97 (100)	608 (99)	489 (99)
C(24)	3489 (19)	−1169 (6)	2822 (19)	653 (78)	551 (79)	662 (77)	192 (66)	307 (67)	225 (66)
C(25)	4929 (17)	−912 (5)	51 (19)	557 (66)	507 (67)	695 (76)	144 (59)	350 (61)	71 (59)
C(26)	4156 (23)	−1289 (7)	−1524 (23)	796 (101)	847 (107)	772 (100)	−62 (86)	328 (82)	−342 (85)
C(27)	3616 (14)	636 (5)	−4901 (15)	475 (57)	545 (65)	504 (57)	99 (56)	316 (49)	15 (55)
C(28)	511 (13)	1647 (4)	−5966 (13)	449 (56)	493 (60)	283 (49)	−174 (51)	183 (45)	−106 (44)
C(29)	−912 (15)	1909 (5)	−5638 (13)	536 (62)	505 (63)	319 (51)	7 (53)	261 (49)	136 (49)
C(30)	−4705 (13)	2159 (4)	−5512 (14)	405 (56)	520 (62)	371 (53)	63 (40)	244 (48)	−58 (48)
C(31)	−5715 (15)	2644 (4)	−5536 (13)	577 (66)	467 (62)	339 (53)	198 (55)	188 (51)	96 (46)
C(32)	−3296 (19)	2335 (5)	−721 (16)	874 (91)	521 (70)	464 (63)	100 (64)	401 (66)	21 (51)
C(33)	−475 (16)	2473 (4)	−5057 (17)	637 (61)	424 (61)	705 (69)	−13 (53)	522 (62)	80 (53)
C(34)	1545 (30)	3049 (6)	−3115 (24)	1476 (171)	694 (91)	907 (108)	−518 (108)	740 (120)	−547 (90)
C(35)	−7099 (14)	2829 (4)	−7321 (15)	481 (62)	485 (63)	479 (59)	29 (50)	294 (52)	106 (51)
C(36)	−9413 (22)	3423 (8)	−8713 (22)	642 (91)	1127 (134)	725 (98)	436 (96)	33 (76)	64 (92)

	x	y	z	U_{iso}		x	y	z	U_{iso}
Mg^{2+}	96 (4)	678 (0)	−757 (4)	416 (8)	C(9)	2634 (13)	−172 (4)	−698 (14)	387 (22)
N(1)	−1168 (10)	424 (3)	594 (10)	356 (17)	C(10)	2888 (13)	72 (4)	−2002 (14)	391 (23)
N(2)	1484 (11)	−21 (3)	−135 (11)	383 (19)	C(11)	2037 (13)	507 (4)	−2973 (13)	375 (21)
N(3)	733 (10)	751 (3)	−2773 (10)	368 (17)	C(12)	2313 (12)	777 (4)	−4307 (13)	375 (22)
N(4)	−1902 (10)	1269 (3)	−2118 (10)	315 (16)	C(13)	1112 (13)	1196 (4)	−4857 (13)	363 (21)
C(1)	−2408 (12)	701 (4)	794 (12)	358 (20)	C(14)	231 (12)	1164 (4)	−3852 (12)	345 (20)
C(2)	−2736 (13)	442 (4)	2126 (14)	426 (22)	C(15)	−968 (13)	1565 (4)	−4181 (13)	384 (22)
C(3)	−1634 (13)	32 (4)	2762 (14)	418 (23)	C(16)	−1983 (12)	1612 (4)	−3352 (12)	326 (20)
C(4)	−637 (13)	24 (4)	1780 (14)	413 (23)	C(17)	−3193 (13)	2059 (4)	−3568 (14)	385 (22)
C(5)	637 (14)	−331 (4)	2034 (14)	438 (23)	C(18)	−3822 (14)	1928 (4)	−2197 (13)	398 (22)
C(6)	1633 (13)	−353 (4)	1145 (14)	395 (22)	C(19)	−2947 (13)	1416 (4)	−1431 (13)	384 (22)
C(7)	2956 (14)	−747 (4)	1455 (14)	466 (25)	C(20)	−3205 (13)	1137 (4)	−165 (13)	370 (22)
C(8)	3578 (14)	−631 (4)	284 (14)	450 (24)					

Two cycles of full-matrix least-squares refinement {weight $= [1/\sigma(F_o)]\exp[a(\sin \theta / \lambda)^2]$, $a = 10$ Å^2 (Dunitz & Seiler, 1973)} yielded a final R of 0·077 for the 1901 reflexions with $|F_o| > 2·5 \, \sigma(|F_o|)$. The expectation value of R is 0·09. Final positional and thermal parameters are given in Table 1.*

Discussion. Fig. 1 shows the molecule projected on the plane of N(1), N(2) and N(3). Derived parameters (interatomic distances and angles, calculated H positions) are not listed here, but are recorded elsewhere (Kratky, 1976).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32132 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
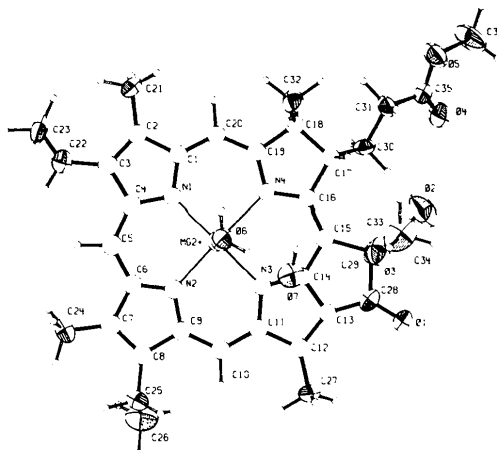

Fig. 1. Projection of the methylchlorophyllide A molecule on the plane of N(1), N(2) and N(3). C(33) is hidden behind C(34) and O(3).
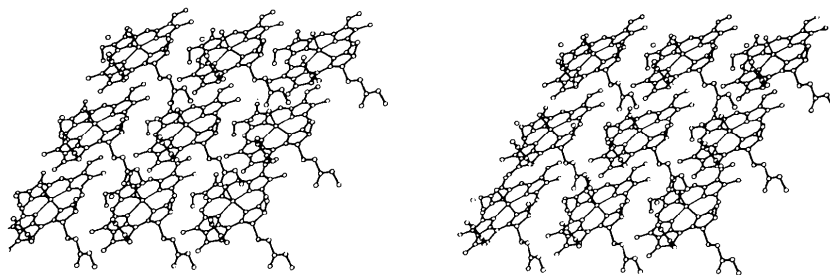
Fig. 2. Packing of methylchlorophyllide A molecules in a two-dimensional layer. The projection is down **b**; **a** runs right to left, and **c** (the propagation direction of the one-dimensional stacks) upwards at an angle turned 30° clockwise from the vertical direction.

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)$\cdots$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)$\cdots$O(6), 2·69 Å], to the ether O(3) [O(7)$\cdots$O(3), 3·05 Å] and to the propionic acid ester carbonyl O(4) of the molecule related by the [101] translation [O(7)$\cdots$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 dif-ferent 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.