The Crystal Structure of the Pyrimidine Analogue Calcium 5-Ethylidenehydroorotate · 1.5 Hydrate, a Photoproduct of Ethylorotate

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5-Ethylidenehydroorotate, Calcium-Salt · 1,5-Hydrate, X-Ray Structure

X-ray diffraction methods have been employed to establish the crystal structure of a new, unusual pyrimidine analogue, 5-ethylidenehydroorotate, obtained by a photochemical rearrangement of 5-ethylorotate. Crystals of the calcium salt of the title compound are monoclinic, space group Pc, cell constants $a=14.631$, $b=10.038$, $c=19.168$ Å, $\beta=137.7°$, and contain four molecules, two cations and three water molecules per asymmetric unit. The structure was solved by direct methods and refined to $R=5.2\%$ on the basis of 2653 diffractometer measured data. The four independent molecules represent two pairs of enantiomers with slightly differing conformations linked together by an intricate system of hydrogen bonding and Ca^{2+}-coordination (pentagonal bipyrimidal). The structure of the compound in aqueous medium, established by spectral methods, is the same as that in the crystal.

Introduction

We have shown elsewhere[1] that 5-ethylorotate in aqueous medium undergoes an unusual photochemical rearrangement, *via* two different pathways, to form 5-ethylidenehydroorotate, which in turn can undergo partial thermal regeneration to the parent 5-ethylorotate, and quantitative conversion photochemically to 5-ethyluracil[1]. We describe here the crystal structure of the calcium salt of 5-ethylidenehydroorotate, a new and novel pyrimidine analogue which was shown by spectroscopic methods to remain unchanged when brought into solution.

Experimental

The photoproduct of 5-ethylorotate was purified on PF 254 Silica gel and crystalized from 20% aqueous methanol. The obtained needles have monoclinic lattice symmetry and cell dimesions: $a=14.631(3)$, $b=10.038(3)$, $c=19.168(4)$ Å, and $\beta=137.7(2)°$. The systematic absence hol with $l=$ odd indicated the space group to be either P2/c or Pc. Using the possibility that the molecule had crystallized as the free acid, the size of the unit cell appeared to necessitate the presence of 8 molecules. The data were colledted from a crystal of dimensions $0.1 \times 0.3 \times 0.5$ mm³ using an automatic STOE diffractometer operated in the $\Theta/2\Theta$ scan mode at a rate of $1°\ \text{min}^{-1}$ with CuK_{α} radiation ($\lambda=1.54182$ Å). Background was measured for 10 seconds on the high and low sides of each scan. The data were corrected for Lorentz and polarization factors but not for absorption.

The centric space group P2/c, with only 2 independent molecules, was first tried, as this seemed more likely than Pc with 4 independent molecules. The $|E|$ values displayed a rational dependence with $k=$ odd reflections being weaker than $k=$ even. In addition subsets of reflections were stronger than others in the following way: oee with $k=4\,n$, eeo with $k=4\,n+2$, oeo with $k=4\,n+2$ and eee with $h=4$ n. The origin could not be properly fixed unless all classes of reflections were renormalized to $\langle E^2 \rangle = 1.0$. When this was done reasonable starting sets of phases could be generated by MULTAN[2] or Long's iterative program (REL)[3]. All of the consistent sets yielded only fragments of the structure and would not improve and therefore MULTAN was used in the acentric space group Pc. The most consistent set yielded 50 out of 52 correct atoms for the 4 molecules and two large peaks which were tentatively identified as 2 sodium ions. The initial R factor was 39.6% and two difference Fouriers completed the structure and showed 6 water molecules for a total of 60 atoms.

Full matrix least squares refinement (ORFLS)[4] of the coordinates and temperature factors reduced the R factor to 17.0% but forced the temperature factors of the presumed Na ions to values of -1.3 Å². Examination of the coordination geo-

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Table I. Coordinates and temperature factors.

Temperature factors are in the form $T = \exp(-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl))$.

The B_{ij} are multiplied by 10^4.

Atom	X	Y	Z	B11	B22	B33	B12	B13	B23
O4C	.6644 (6)	−.0031 (5)	.5143 (4)	106 (6)	83 (5)	44 (3)	−4 (5)	60 (4)	0 (3)
C5C	.6184 (7)	−.1443 (7)	.5877 (5)	36 (6)	58 (7)	38 (5)	1 (5)	35 (5)	−4 (4)
C6C	.6551 (7)	−.1598 (7)	.6816 (5)	46 (7)	61 (7)	43 (5)	−1 (5)	40 (5)	−6 (4)
C7C	.5669 (7)	−.0596 (6)	.6771 (5)	59 (8)	51 (7)	35 (4)	0 (6)	41 (5)	2 (4)
O71C	.4428 (5)	−.0690 (5)	.6067 (4)	47 (5)	103 (6)	47 (3)	−7 (4)	34 (4)	−15 (3)
O72C	.6295 (5)	.0327 (5)	.7430 (4)	62 (5)	90 (6)	35 (3)	−15 (4)	35 (3)	−16 (3)
C8C	.5213 (8)	−.2131 (7)	.4997 (6)	54 (7)	80 (8)	29 (4)	0 (6)	31 (5)	3 (5)
C9C	.4309 (9)	−.3176 (8)	.4773 (6)	71 (8)	83 (8)	49 (5)	−14 (7)	41 (6)	−5 (5)
N1D	.8026 (5)	.3372 (6)	.7620 (4)	31 (5)	72 (6)	39 (4)	7 (5)	25 (4)	16 (4)
C2D	.8656 (8)	.4453 (8)	.7727 (6)	51 (8)	76 (8)	35 (5)	18 (6)	30 (5)	15 (5)
O2D	.9777 (5)	.4833 (5)	.8542 (4)	40 (5)	108 (6)	26 (3)	−21 (4)	12 (3)	9 (3)
N3D	.8007 (6)	.5159 (6)	.6811 (4)	49 (6)	67 (6)	28 (3)	0 (4)	30 (4)	12 (3)
C4D	.6921 (7)	.4696 (7)	.5865 (6)	41 (7)	72 (7)	34 (4)	10 (6)	30 (5)	13 (5)
O4D	.6582 (6)	.5259 (5)	.5102 (4)	78 (6)	93 (5)	38 (3)	−9 (5)	43 (4)	4 (3)
C5D	.6167 (7)	.3593 (7)	.5735 (6)	45 (7)	59 (7)	36 (4)	−2 (5)	35 (5)	−1 (4)
C6D	.6611 (6)	.3107 (6)	.6681 (5)	48 (7)	52 (6)	32 (4)	8 (5)	33 (5)	−1 (4)
C7D	.5704 (7)	.3773 (7)	.6752 (5)	46 (7)	85 (8)	25 (4)	22 (6)	25 (5)	16 (5)
O71D	.6053 (6)	.4868 (5)	.7170 (4)	93 (6)	78 (6)	56 (4)	−1 (5)	59 (4)	−16 (3)
O72D	.4641 (4)	.3145 (5)	.6302 (3)	38 (5)	95 (5)	41 (3)	−2 (4)	32 (3)	8 (3)
C8D	.5170 (8)	.3045 (8)	.4801 (6)	54 (8)	93 (8)	41 (5)	−13 (6)	36 (5)	−17 (5)
C9D	.4253 (9)	.1903 (9)	.4491 (6)	79 (9)	83 (8)	48 (5)	−23 (7)	38 (6)	−11 (5)
KA1	.4373 (0)	.1337 (1)	.6922 (0)	49 (1)	72 (1)	36 (1)	1 (1)	32 (1)	1 (1)
KA2	.1659 (1)	−.3875 (1)	.5235 (1)	49 (1)	64 (1)	35 (1)	−3 (1)	31 (1)	−1 (1)
W1	.4087 (5)	−.0415 (5)	.7553 (4)	69 (6)	96 (6)	51 (3)	14 (5)	45 (4)	14 (3)
W2	.3626 (5)	.2967 (5)	.7365 (4)	70 (6)	113 (6)	48 (3)	20 (5)	49 (4)	6 (4)
W3	.2036 (6)	.1378 (6)	.5360 (5)	65 (6)	139 (8)	58 (4)	9 (5)	35 (4)	−39 (5)
W4	.1859 (5)	−.2017 (5)	.4576 (4)	71 (6)	100 (6)	57 (4)	3 (4)	52 (4)	11 (3)
W5	.3981 (5)	−.4035 (5)	.6799 (4)	61 (6)	101 (6)	54 (4)	6 (5)	32 (4)	−22 (4)
W6	.2394 (5)	−.5435 (5)	.4752 (4)	76 (6)	109 (6)	45 (3)	20 (5)	46 (4)	−1 (4)
N1A	.7796 (5)	.3913 (6)	.4291 (5)	36 (6)	61 (6)	36 (4)	−1 (5)	23 (4)	9 (4)
C2A	.7193 (7)	.2824 (7)	.4235 (6)	44 (7)	74 (7)	37 (5)	3 (6)	36 (5)	5 (5)
O2A	.6081 (5)	.2387 (5)	.3400 (4)	50 (5)	98 (6)	36 (3)	−20 (4)	21 (3)	1 (3)
N3A	.7859 (6)	.2225 (6)	.5138 (4)	57 (6)	66 (6)	24 (3)	−7 (5)	25 (4)	−9 (4)
C4A	.8956 (8)	.2763 (7)	.6141 (6)	72 (8)	62 (7)	49 (5)	−12 (6)	55 (6)	−21 (5)
O4A	.9303 (6)	.2275 (4)	.6875 (4)	85 (5)	78 (5)	28 (3)	−17 (4)	43 (3)	−4 (3)
C5A	.9604 (7)	.3924 (7)	.6179 (5)	53 (7)	79 (7)	27 (4)	7 (6)	33 (5)	10 (4)
C6A	.9173 (7)	.4303 (6)	.5182 (5)	64 (8)	51 (6)	27 (4)	0 (6)	29 (5)	4 (4)
C7A	1.0164 (7)	.3649 (6)	.5226 (5)	50 (7)	63 (7)	26 (4)	−13 (6)	26 (5)	0 (4)
O71A	.9912 (6)	.2489 (5)	.4883 (4)	76 (6)	79 (5)	61 (4)	−15 (4)	54 (4)	−26 (3)
O72A	1.1249 (4)	.4273 (5)	.5717 (3)	46 (5)	84 (5)	40 (3)	5 (4)	34 (3)	7 (3)
C8A	1.0661 (8)	.4451 (7)	.7119 (6)	85 (9)	60 (7)	56 (5)	−1 (6)	58 (6)	−2 (5)
C9A	1.1586 (8)	.5555 (8)	.7404 (6)	71 (8)	81 (8)	47 (5)	−11 (7)	44 (6)	−3 (5)
N1B	.8216 (6)	−.0970 (5)	.4533 (4)	52 (6)	60 (6)	31 (3)	4 (4)	31 (4)	6 (3)
C2B	.7483 (7)	−.1934 (7)	.4423 (5)	30 (7)	57 (7)	27 (4)	3 (5)	23 (5)	−2 (4)
O2B	.6299 (5)	−.2212 (5)	.3601 (4)	48 (5)	86 (5)	37 (3)	−7 (4)	28 (4)	4 (3)
N3B	.8090 (6)	−.2593 (6)	.5305 (5)	58 (6)	62 (6)	28 (3)	−8 (5)	28 (4)	−1 (3)
C4B	.9214 (8)	−.2130 (7)	.6325 (6)	46 (7)	63 (7)	29 (4)	−4 (5)	28 (5)	−13 (4)
O4B	.9463 (6)	−.2591 (5)	.7030 (4)	75 (5)	92 (5)	31 (3)	−8 (5)	40 (4)	0 (3)
C5B	.9988 (7)	−.1048 (7)	.6406 (5)	47 (7)	74 (7)	23 (4)	0 (6)	25 (5)	1 (4)
C6B	.9663 (6)	−.0890 (6)	.5429 (5)	40 (6)	45 (6)	31 (4)	2 (5)	29 (4)	0 (4)
C7B	1.0454 (7)	−.1936 (7)	.5456 (5)	49 (7)	59 (7)	26 (4)	−1 (5)	30 (5)	6 (4)
O71B	1.1729 (5)	−.1939 (5)	.6176 (4)	52 (5)	87 (5)	42 (3)	−4 (4)	35 (3)	−16 (3)
O72B	.9767 (5)	−.2768 (5)	.4721 (4)	69 (5)	79 (5)	41 (3)	−4 (4)	41 (4)	−20 (3)
C8B	1.0920 (8)	−.0381 (7)	.7291 (6)	59 (8)	65 (7)	38 (5)	0 (6)	35 (5)	−3 (5)
C9B	1.1779 (9)	.0703 (9)	.7501 (7)	83 (9)	94 (9)	50 (5)	−21 (7)	47 (6)	−25 (6)
N1C	.7993 (6)	−.1396 (5)	.7768 (4)	56 (6)	71 (6)	31 (3)	3 (5)	34 (4)	2 (4)
C2C	.8666 (7)	−.0394 (7)	.7827 (6)	43 (7)	68 (7)	37 (5)	0 (6)	26 (5)	8 (5)
O2C	.9773 (6)	.0016 (5)	.8610 (4)	68 (6)	84 (5)	28 (3)	−18 (4)	20 (3)	7 (3)
N3C	.8007 (6)	.0159 (6)	.6850 (5)	62 (6)	62 (6)	33 (4)	0 (5)	37 (4)	11 (3)
C4C	.6957 (7)	−.0413 (7)	.5932 (6)	45 (7)	63 (7)	36 (5)	6 (6)	31 (5)	12 (5)

metry and consideration of charge led to the conclusion that the sodiums were probably calciums eluted from the Silica gel material. The 4 negative charges on the carboxyl groups had to be balanced by 4 positive charges, and since only 2 ions were evident, as well as high density by the behavior of the temperature factors, they were most likely Ca^{2+} ions. When this was changed the *R* factor reduced dramatically to 9.6% with temperature factors for the calcium ions of 2.2 Å^2. A subsequent analysis of the crystal confirmed that it was the calcium salt (see below).

Anisotropic refinement of the non-hydrogen atoms, plus assignment to the remaining hydrogen atoms either by difference Fourier or geometrically by hydrogen bonding, with temperature factors of the atoms to which they were attached and correction of 21 reflections for secondary extinction effects[5], reduced the *R* factor to 5.2%. The atomic coordinates of the non-hydrogen atoms are listed in Table I and observed and calculated structure factors are given in Table II[6].

Results and Discussion

The most complex aspect of the structure is the presence of 4 independent, chiral molecules. Space group Pc has a mirror plane in he form of a c-glide and this allows both enantiomorphs to reside in the crystal. But this does not explain the 4 different molecules in the asymmetric unit unrelated by a glide plane. Tables III and IV show the average bond lengths and angles of molecules A + B and C + D. From this it is clear that there is a different electronic configuration between these two. The C(2) – N(3) bond for A/B has more double bond character than in C/D, being 0.074 Å shorter than in C/D. In C/D the C(4) – O(4) bond is longer by 0.078 Å, indicating more single bond character than in A/B which is purely double. There is also a difference in the C(5) – C(6) and C(6) – C(7) bonds which is reflected in the bond angles C(5) – C(6) – N(1) and N(1) – C(6) – C(7). These values have higher standard deviations and may not be significant, but any differences may be due to packing forces which are very important in this structure. While the electronic configuration can account for half the result, another effect is needed. This can be seen in Table V, which lists the dihedral angles of the 4 molecules. The most crucial angles are the ones about the C(6) – C(7) bond and are N(1) – C(6) – C(7) – O(71), N(1) – C(6) – C(7) – O(72), C(5) – C(6) – C(7) – O(71), and C(5) – C(6) – C(7) – O(72). Ignoring the signs of the angles due to the glide plane, it becomes clear that molecules A/D and B/C have similar conformations related by a 30° rotation about the C(6) – C(7) bond. This can also be seen in Fig. 1 as the bond about C(6) – C(7) is clearly rotated. The reason for this is in the calcium coordination geometry (Fig. 2 and Table VI). Carboxyl group C is related to calcium 1 in the same way as carboxyl group B is related to calcium 2, while O(72)D and O(72)A are related in the same way to calcium 1 and 2, respectively. This explains the similarity in the conformation about C(6) – C(7) of A/D and B/C. With electronic differences and conformational changes we then can have 4 different molecules for each combination.

Table III. Average bond lengths and standard deviations.

Bond	Molecules A+B	 C+D
N1–C2	1.349 (9)	1.344 (10)
C2–O2	1.239 (5)	1.212 (18)
C2–N3	1.356 (9)	1.430 (10)
N3–C4	1.412 (7)	1.334 (6)
C4–O4	1.197 (11)	1.275 (11)
C4–C5	1.480 (11)	1.462 (15)
C5–C6	1.558 (12)	1.473 (15)
C6–N1	1.432 (6)	1.451 (7)
C5–C8	1.334 (7)	1.336 (7)
C8–C9	1.491 (14)	1.498 (16)
C6–C7	1.520 (18)	1.584 (12)
C7–O71	1.262 (7)	1.227 (7)
C7–O72	1.268 (7)	1.257 (7)

Table IV. Average bond angles and standard deviations.

Angles	Molecules A+B	 C+D
C2–N1–C6	123.5 (16)	121.0 (11)
N1–C2–O2	123.7 (10)	125.8 (7)
N1–C2–N3	116.4 (6)	116.5 (10)
O2–C2–N3	119.9 (9)	118.2 (6)
C2–N3–C4	125.9 (6)	123.5 (6)
N3–C4–C5	114.1 (6)	118.7 (9)
N3–C4–O4	120.6 (7)	118.5 (7)
O4–C4–C5	125.4 (7)	122.8 (7)
C4–C5–C6	116.1 (19)	115.9 (8)
C4–C5–C8	117.7 (14)	118.7 (7)
C6–C5–C8	125.7 (8)	124.8 (7)
C5–C8–C9	126.8 (11)	128.0 (7)
C5–C6–C7	108.4 (14)	109.0 (6)
C5–C6–N1	108.4 (10)	113.4 (6)
N1–C6–C7	114.0 (6)	109.9 (5)
C6–C7–O71	120.0 (6)	118.7 (10)
C6–C7–O72	117.7 (6)	116.0 (10)
O71–C7–O72	122.4 (6)	125.2 (20)

Table V. Dihedral angles * and standard deviations.

Angle	Molecules A	B	C **	D **
N1–C2–N3–C4	15(2)	19(1)	−13(1)	−9(1)
N1–C6–C5–C4	30(1)	44(1)	−35(1)	−26(1)
N1–C6–C7–O71	−30(1)	177(1)	−174(1)	38(1)
N1–C6–C7–O72	151(1)	−2(1)	11(1)	−146(1)
N1–C6–C5–C8	−161(1)	−140(1)	146(1)	151(1)
O2–C2–N3–C4	−165(1)	−158(1)	163(1)	167(1)
O2–C2–N1–C6	−167(1)	−165(1)	166(1)	169(1)
C2–N3–C4–C5	−16(2)	−18(2)	18(1)	14(2)
C2–N3–C4–O4	165(1)	161(1)	−164(1)	−166(1)
C2–N1–C6–C5	−33(1)	−48(1)	41(1)	33(1)
C2–N1–C6–C7	86(1)	74(1)	−81(1)	−90(1)
N3–C4–C5–C6	−8(1)	−15(1)	8(1)	4(2)
N3–C4–C5–C8	−179(1)	169(1)	−173(1)	−173(1)
N3–C2–N1–C6	13(1)	18(1)	−18(2)	−16(1)
O4–C4–C5–C8	0(2)	−10(2)	9(2)	8(2)
O4–C4–C5–C6	171(1)	166(1)	−170(1)	−175(1)
C4–C5–C8–C9	174(1)	179(1)	−179(1)	−179(1)
C4–C5–C6–C7	−94(1)	−81(1)	88(1)	96(1)
C5–C6–C7–O71	91(1)	−62(1)	61(1)	−86(1)
C5–C6–C7–O72	−88(1)	119(1)	−114(1)	89(1)
C9–C8–C5–C6	4(2)	4(2)	0(2)	4(2)
C8–C5–C6–C7	76(1)	95(1)	−91(1)	−86(1)

* Definition: The angles A–B–C–D are defined as zero when the bonds A–B and C–D are cis planar. They are counted positive when, looking along the central B–C bond, the far bond is rotated clockwise with respect to the near bond.

** These are molecules related by a glide plane and the sign of the angles are therefore reversed.

Table VI. Calcium coordination system.

a)
Distances to calcium 1 (Ka 1)

Atom	Distance
O2B	2.379
W1	2.341
W2	2.443
W3	2.349
O71C	2.650
O72C	2.416
O72D	2.355

Distances to calcium 2 (Ka 2)

Atom	Distance
O2D	2.414
W4	2.390
W5	2.344
W6	2.437
O71B	2.601
O72B	2.415
O72A	2.343

b)
Angles about Ka 1

	Atoms	Angles	
(1)	O72D–O2B	85.7	
	O72D–W1	178.3	
	O72D–W2	86.8	
	O72D–W3	88.4	
	O72D–O71C	100.8	
	O72D–O72C	87.1	
(2)	W1–O2B	93.6	
	W1–W2	91.5	
	W1–W3	91.4	
	W1–O71C	80.9	
	W1–O72C	94.3	
(3)	W2–O2B	70.7	total 361.7°
	O2B–O72C	75.4	
	O72C–O71C	50.9	
	O71C–W3	84.6	
	W2–W3	80.1	
(4)	O2B–W3	150.4	
	O2B–O71C	125.0	
	W2–O71C	162.7	
	W3–O72C	133.2	
	W2–O72C	145.9	

Angles about Ka 2

	Atoms	Angles	
(1)	O72A–O2D	81.0	
	O72A–W4	174.4	
	O72A–W5	89.6	
	O72A–W6	87.3	
	O72A–O71B	102.1	
	O72A–O72B	88.6	
(2)	W4–O2D	93.7	
	W4–W5	95.8	
	W4–W6	92.3	
	W4–O71B	80.0	
	W4–O72B	88.7	
(3)	W6–O2D	67.5	total 361.4°
	O2D–O72B	79.1	
	O72B–O71B	52.0	
	O71B–W5	83.6	
	W5–W6	79.2	
(4)	O2D–W5	145.7	
	O2D–O71B	130.6	
	W6–O71B	160.3	
	W5–O72B	133.9	
	W6–O72B	146.6	

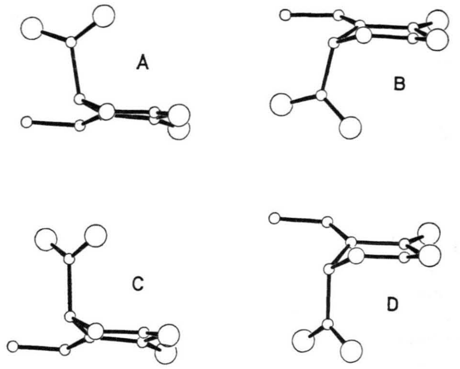

Fig. 1. Representation of the four ethylidenehydroorotate molecules present in one asymmetric unit o=C, O=o. Projections are on the plane through atoms N(3), C(6), C(7).

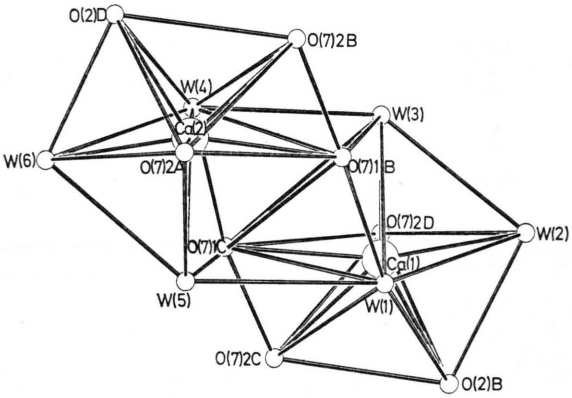

Fig. 2. The pentagonal bipyramidal coordination around the two calcium ions.

A detailed analysis of the structure indicated the exocyclic double bond to be at C(5) – C(8), making the ring somewhat strained since C(6) is tetrahedral. The deviations of the atoms from the least squares planes of atoms N(1), C(2), N(3) and C(4) are given in Table VII. The maximum deviation of atoms N(1), C(2), N(3) and C(4) is 0.076 Å, as compared to dihydrouridine[7] with 0.072 Å. As in dihydrouridine, C(5) is practically in the plane, with a maximum deviation of 0.155 Å, while C(6) is very much out of the plane, or puckered, with a minimum deviation of 0.490 Å and maximum of 0.664 Å. Atoms O(4) and O(2) are also somewhat out of the plane by about 0.2 Å, while C(8) and C(9) are more in the plane due to the exocyclic carbon-carbon double bond. Atom C(9) can be said to be *trans* to C(4) and *cis* to C(6). It cannot be *cis* to C(4) for then the methyl hydrogens could be too close to O(4).

Table VII. Deviations of atoms from individual least squares planes defined by atoms N1, C2, N3, C4.

Atom	Molecules A	B	C	D
N1	0.027	0.035	−0.027	−0.019
C2	−0.057	−0.074	0.054	0.037
O2	−0.234	−0.360	0.270	0.224
N3	0.059	0.076	−0.057	−0.039
C4	−0.029	−0.037	0.030	0.020
O4	−0.172	−0.228	0.229	0.217
C5	0.091	0.076	−0.155	−0.148
C6	0.490	0.664	−0.585	−0.479
C7	1.979	2.196	−2.172	−2.042
O71	2.727	2.871	−2.820	−2.714
O72	2.446	2.731	−2.699	−2.463
C8	0.033	−0.239	0.056	0.053
C9	0.242	−0.169	−0.096	−0.077

Returning to Table VI and Fig. 2, the calcium coordination system can be described as a slightly distorted pentagonal bipyramid. This has been observed recently in calcium hydroxylcarboxylate complexes[8, 9]. The distortion is due to the forced presence of both carboxyl oxygens from molecule C and molecule D into the system of calcium 1 and 2

Table VIII. Close interatomic contacts.

a) Intermolecular contacts

Atom	Atom	d[Å]
N1A	O71D^{a}	3.03
O4A	N3C^{b}	2.82
O71A	N1C^{c}	2.95
O72A	O2D^{a}	3.09
N3A	O4C^{b}	2.88
N1B	O72C^{c}	2.79
O2B	O72C^{c}	2.93
N3B	O4C^{b}	3.19
N3B	O4D^{d}	2.90
O4B	N3D^{d}	2.91
O72B	N1D^{c}	2.81
O72B	O2D^{c}	3.07

b) Water contacts

Atom	Atom	d[Å]
W1	O2A^{e}	2.84
W1	O71B^{f}	2.79
W2	O2B^{e}	2.79
W2	O72A^{b}	2.75
W2	W3^{b}	3.08
W3	O71A^{b}	2.74
W3	O2C^{g}	2.78
W4	O2C^{g}	2.91
W4	O71C^{b}	2.86
W5	O2A^{e}	2.77
W5	O71D^{h}	2.78
W5	W6^{b}	3.06
W6	O2D^{g}	2.70
W6	O72D^{h}	2.69

Transformations

a) x, 1−y, −1/2+z
b) x, y, z
c) x, −y, −1/2+z
d) x, 1+y, z
e) x, −y, 1/2+z
f) −1+x, y, z
g) −1+x, −y, −1/2+z
h) x, −1+y, z

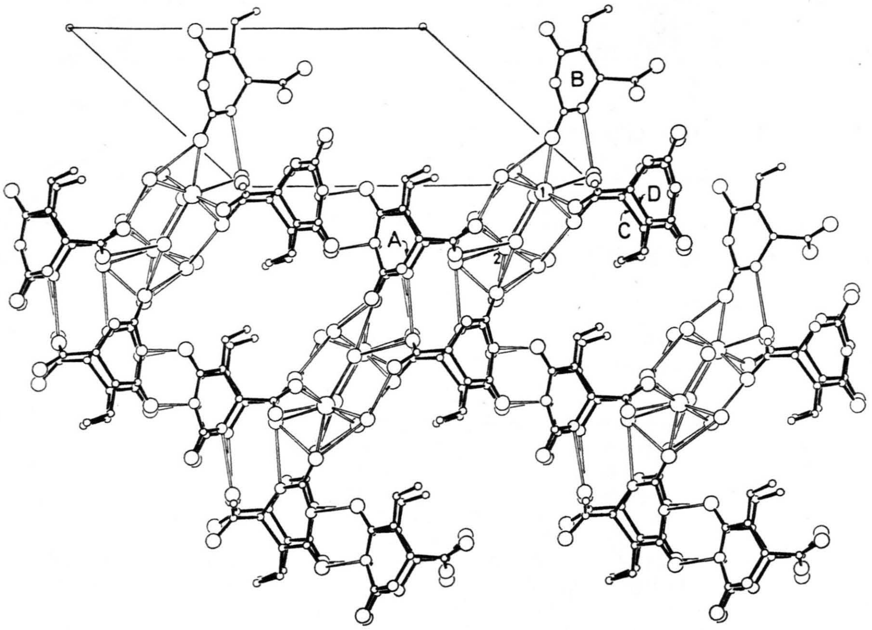

Fig. 3. View of the crystal structure in the projection along the *b*-axis. Note regions of hydrophilic character (calcium ions and water molecules) and of hydrophobic character (ethylidene group).

respectively. These are reflected in a distortion of the angles about the calcium atoms, as can be seen in Table VI. Although the pentagonal base is slightly distorted, it is fairly flat and its angles sum to 361.7° and 361.4° as compared to 360° for perfect planarity.

The hydrogen bonding system is quite complex and is shown in Fig. 3 and Table VIII. The calcium and water coordination system strongly bonds the structure together as well as base pairing N(3) to O(4) for A/C and B/D pairs. In addition base stacking interactions are present but at only 5 Å separation and are therefore weak. This is probably due to the tetrahedral C(6) with its carboxyl group, which deviates over 2 Å from the plane of the base. A hydrophobic pocket is also seen between methyl groups.

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