

déduits par symétrie des deux atomes de cadmium indépendants sont approximativement coplanaires exceptés Cd(2ⁱ) et Cd(2ⁱⁱⁱ) qui se disposent de part et d'autre du plan moyen de la Fig. 3. Les écarts par rapport à ce plan sont donnés dans le Tableau 3. (ii) Les groupements SO₄ sont situés de part et d'autre du plan (Figs. 1, 2, 3), assurant la liaison entre les couches.

Tableau 3. Distances (Å) des atomes au plan (1 $\bar{1}$ 0)

Cd(2 ^{iv})	-0,040	Cd(1 ⁱ)	0,227
Cd(2 ⁱⁱ)	0,040	Cd(1 ⁱⁱⁱ)	-0,227
Cd(1 ⁱⁱ)	-0,099	Cd(2 ⁱ)	1,733
Cd(1 ^{iv})	0,099	Cd(2 ⁱⁱⁱ)	-1,733

La Fig. 2 reproduit les polyèdres dans la maille, en excluant les octaèdres relatifs à Cd(2ⁱ) et Cd(2ⁱⁱⁱ) afin de mieux dégager la direction générale de la famille de couches approximativement parallèles à (1 $\bar{1}$ 0). Les deux octaèdres manquants appartiennent à l'autre famille de couches identiques, approximativement parallèles à (110). L'édifice structural peut donc être décrit à partir de l'ensemble élémentaire de quatre octaèdres relatifs à Cd(1ⁱ), Cd(1ⁱⁱⁱ), Cd(2ⁱ), Cd(2ⁱⁱⁱ) qui se déduisent d'ailleurs deux à deux par deux centres de symétrie situés au milieu des arêtes O(6ⁱ)-O(6^{iv}) et O(5ⁱ)-O(5ⁱⁱⁱ) (Fig. 1). C'est la reproduction de cet

ensemble élémentaire: suivant [001] par translation de **c**; suivant [110] par le plan *n* et par translation **a**+**b**, qui conduit à la formation des deux familles de couches enchevêtrées vues en perspective sur la Fig. 4.

Les distortions par rapport au type structural Cd(OH)₂ (Bertrand & Dusausoy, 1970) sont beaucoup plus importantes que pour Cd₂(OH)₂SO₄-β. Ce dernier conservait, bien que déformés, les plans cationiques. Dans la variété γ, ces plans se scindent en deux directions et deviennent déficitaires en atomes de cadmium parce que deux sur huit se placent de part et d'autre, conduisant à la formation de vides importants dans chaque feuillet (Fig. 3). En remplaçant les atomes de cadmium (2ⁱ) et (2ⁱⁱⁱ) dans le plan de la figure, on retrouverait l'aspect du feuillet caractéristique de la variété β.

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The Crystal Structure of Calcium Hydrogen Dihomophthalate Pentahydrate, Ca(C₉H₇O₄)₂·5H₂O

BY M. P. GUPTA AND N. PRASAD

Department of Physics, Ranchi University, Ranchi-834008, India

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The structure of calcium hydrogen dihomophthalate pentahydrate has been determined and refined by least squares to an *R* of 0.104. There are two independent homophthalic acid residues in the asymmetric unit of a centrosymmetric triclinic cell [*a* = 19.58 (2), *b* = 5.79 (1), *c* = 9.95 (1) Å, α = 92.40, β = 103.42, γ = 99.44°] and in both only one of the two carboxyl groups is ionized. The molecules are held together by van der Waals contacts, metal-oxygen linkages, hydrogen bonds of 2.59 and 2.60 Å between carboxyl O atoms of adjacent homophthalic acid species, and hydrogen bonds, ranging from 2.62 to 3.08 Å, from the five water molecules. The corresponding carboxyl groups in the homophthalic acid residues are rotated out of the planes of their respective central aromatic rings by 12.2 and 11.7°, and 101.7 and 105.4°. There is eightfold coordination around the Ca with an average Ca-O distance of 2.48 Å.

Introduction

A determination of the crystal structure of Ca(C₉H₇O₄)₂·5H₂O was undertaken because of interest in its scheme of hydrogen bonding. Moreover, the formula for the compound could be either Ca(C₉H₇O₄)₂·5H₂O or Ca(C₉H₆O₄)(C₉H₈O₄)·5H₂O, each representing

a different structure. A somewhat similar case was reported for the K salt of homophthalic acid (Gupta & Dubey, 1972).

Crystal data

Triclinic, *a* = 19.58 (2), *b* = 5.79 (1), *c* = 9.95 (1) Å, α = 92.40, β = 103.42, γ = 99.44°, *D_m* = 1.547, *D_c* = 1.552 g

cm^{-3} , $Z=2$, space group $P\bar{1}$, $\mu(\text{Cu } K\alpha)=33.9 \text{ cm}^{-1}$.

In the asymmetric unit are present either two independent, singly ionized homophthalic acid residues ($\text{C}_9\text{H}_7\text{O}_4$) or one homophthalic acid molecule ($\text{C}_9\text{H}_8\text{O}_4$) and its doubly ionized residue ($\text{C}_9\text{H}_6\text{O}_4$).

1752 independent reflexions were collected with Cu K radiation from a single crystal ($0.05 \times 0.03 \times 0.01 \text{ cm}$) by Weissenberg photography. Intensities were estimated visually and brought to an absolute scale by statistical methods.

Structure determination and refinement

The crystal was solved from a Patterson synthesis and packing considerations. Although Ca atoms were located, a Fourier synthesis based on signs fixed by Ca alone failed to refine. Four O atoms were then located from a further study of the Patterson map and these, together with the Ca atoms located earlier, determined the signs of 1100 reflexions to give the positions of 23 atoms in the organic part of the structure. Successive Fourier refinements revealed the positions of all the atoms in the asymmetric unit except the H atoms. Full-matrix least-squares analysis (Busing, Martin & Levy, 1962) with anisotropic temperature factors for all the

atoms and application of an extinction correction (Zachariasen, 1967) reduced R to 0.104. H atoms were not located and their contributions are not included in the calculated structure factors.* The numbering scheme is given in Fig. 3. The positional and thermal parameters are in Table 1. Bond lengths and angles are in Table 2. Equations to the least-squares planes through the various atoms in the two independent molecules and deviations of atoms from these planes are in Table 3. The Ca–O ionic linkages and O–Ca–O angles are in Table 4. A list of several short intermolecular contact distances is given in Table 5.

Molecular structure, metal–oxygen polyhedra and environments of the water molecules

(a) Molecular structure

The bond lengths and angles in the homophthalic acid residues are similar to the values reported earlier

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31958 (27 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters with standard deviations in parentheses*

The anisotropic temperature coefficients are in the form: $T_i = \exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. All values are $\times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	254 (1)	−1241 (6)	2076 (2)	4 (2)	44 (30)	38 (8)	−2 (5)	−3 (2)	−4 (10)
<i>W</i> (1)	683 (4)	1466 (17)	416 (9)	9 (2)	606 (45)	88 (12)	2 (7)	−7 (4)	−4 (16)
<i>W</i> (2)	619 (5)	2350 (18)	3560 (12)	12 (2)	136 (45)	146 (15)	4 (7)	−17 (4)	−28 (16)
<i>W</i> (3)	395 (5)	7204 (18)	4296 (19)	18 (2)	241 (47)	50 (9)	21 (8)	−1 (4)	5 (16)
<i>W</i> (4)	836 (4)	856 (15)	7379 (10)	8 (2)	17 (37)	108 (11)	12 (6)	4 (4)	−26 (16)
<i>W</i> (5)	413 (4)	5288 (16)	8357 (10)	7 (2)	67 (40)	117 (12)	4 (6)	−1 (3)	29 (15)
Residue I									
O(1)	968 (4)	−3604 (15)	1164 (8)	5 (2)	165 (40)	72 (11)	3 (6)	−4 (3)	−46 (16)
O(2)	1669 (4)	−1067 (14)	2779 (8)	10 (2)	38 (38)	64 (9)	−7 (6)	−1 (3)	−29 (16)
O(3)	1988 (4)	228 (17)	50 (10)	1 (2)	227 (45)	138 (13)	−18 (6)	−4 (4)	18 (16)
O(4)	2961 (4)	2537 (16)	−295 (9)	7 (2)	107 (40)	118 (13)	−6 (6)	7 (4)	39 (16)
C(1)	1570 (6)	−2657 (26)	1882 (13)	5 (3)	268 (70)	82 (16)	1 (9)	−1 (5)	−35 (24)
C(2)	2188 (6)	−3735 (25)	1515 (15)	13 (4)	114 (66)	123 (20)	8 (11)	−6 (6)	−2 (24)
C(3)	2923 (6)	−2165 (24)	2070 (13)	16 (3)	62 (58)	77 (16)	16 (9)	12 (6)	−7 (21)
C(4)	3421 (6)	−2955 (27)	3085 (15)	10 (4)	264 (72)	96 (17)	30 (12)	6 (6)	4 (25)
C(5)	4117 (6)	−1803 (28)	3582 (17)	3 (3)	269 (80)	162 (22)	−6 (11)	−7 (6)	48 (28)
C(6)	4354 (7)	210 (28)	2999 (18)	10 (3)	185 (80)	187 (25)	2 (11)	−4 (7)	−15 (32)
C(7)	3867 (5)	1076 (23)	1935 (14)	2 (3)	91 (60)	125 (18)	15 (8)	6 (5)	48 (23)
C(8)	3152 (6)	−1010 (25)	1458 (14)	11 (3)	155 (60)	88 (17)	23 (9)	1 (5)	−2 (22)
C(9)	2633 (6)	957 (25)	386 (17)	7 (3)	87 (65)	179 (23)	2 (9)	−2 (6)	21 (26)
Residue II									
O(5)	2785 (5)	1358 (19)	4492 (10)	23 (3)	280 (48)	106 (13)	35 (8)	8 (6)	−48 (17)
O(6)	2030 (5)	3531 (19)	4975 (12)	18 (3)	270 (50)	178 (16)	33 (9)	−28 (5)	−136 (20)
O(7)	1301 (4)	6675 (16)	6818 (10)	8 (2)	197 (42)	117 (13)	30 (7)	13 (4)	38 (16)
O(8)	1994 (4)	4391 (16)	8057 (9)	8 (2)	192 (42)	80 (11)	−9 (7)	2 (4)	64 (16)
C(10)	2625 (6)	3057 (25)	5237 (15)	6 (3)	191 (68)	115 (19)	15 (11)	−5 (6)	4 (18)
C(11)	3239 (6)	4243 (21)	6383 (9)	5 (3)	154 (59)	35 (12)	−13 (9)	−10 (5)	−30 (19)
C(12)	3858 (5)	3224 (22)	6696 (13)	12 (4)	136 (64)	81 (16)	19 (11)	−2 (5)	−10 (23)
C(13)	4429 (7)	4269 (28)	7733 (13)	12 (4)	314 (80)	128 (20)	−5 (12)	−14 (6)	−24 (30)
C(14)	4392 (8)	6319 (32)	8512 (16)	19 (5)	415 (80)	100 (20)	−2 (14)	−1 (8)	−27 (30)
C(15)	3776 (7)	7325 (30)	8193 (17)	14 (5)	311 (72)	54 (16)	1 (6)	1 (6)	−63 (24)
C(16)	3182 (6)	6257 (24)	7147 (14)	2 (3)	69 (60)	87 (16)	−27 (8)	−9 (5)	−2 (22)
C(17)	2539 (6)	7452 (23)	6859 (13)	13 (3)	59 (60)	94 (16)	5 (9)	15 (6)	17 (22)
C(18)	1893 (5)	5969 (23)	7268 (12)	2 (3)	106 (58)	58 (14)	−23 (8)	−9 (5)	−36 (22)

Table 2. Bond lengths (Å) and angles (°) with their *e.s.d.*'s in parentheses

Residue I		Residue II	
C(1)–O(1)	1.25 (2)	C(18)–O(8)	1.28 (1)
C(1)–O(2)	1.21 (1)	C(18)–O(7)	1.24 (1)
C(1)–C(2)	1.55 (2)	C(18)–C(17)	1.55 (2)
C(2)–C(3)	1.53 (2)	C(17)–C(16)	1.51 (2)
C(3)–C(4)	1.38 (2)	C(16)–C(15)	1.40 (2)
C(4)–C(5)	1.38 (2)	C(15)–C(14)	1.40 (2)
C(5)–C(6)	1.38 (2)	C(14)–C(13)	1.41 (2)
C(6)–C(7)	1.42 (2)	C(13)–C(12)	1.37 (2)
C(7)–C(8)	1.41 (2)	C(12)–C(11)	1.41 (2)
C(8)–C(3)	1.41 (2)	C(11)–C(16)	1.39 (2)
C(8)–C(9)	1.52 (2)	C(11)–C(10)	1.50 (2)
C(9)–O(3)	1.23 (2)	C(10)–O(6)	1.21 (2)
C(9)–O(4)	1.31 (2)	C(10)–O(5)	1.32 (2)
O(1)–C(1)–O(2)	124.0 (1.2)	O(7)–C(18)–O(8)	126.2 (1.2)
O(1)–C(1)–C(2)	113.2 (1.2)	O(8)–C(18)–C(17)	114.1 (1.2)
O(2)–C(1)–C(2)	122.7 (1.2)	O(7)–C(18)–C(17)	119.3 (1.2)
C(1)–C(2)–C(3)	113.2 (1.2)	C(18)–C(17)–C(16)	111.7 (1.2)
C(2)–C(3)–C(4)	118.9 (1.2)	C(17)–C(16)–C(15)	117.7 (1.2)
C(2)–C(3)–C(8)	119.2 (1.2)	C(17)–C(16)–C(11)	118.8 (1.2)
C(3)–C(4)–C(5)	124.2 (1.3)	C(16)–C(15)–C(14)	120.8 (1.2)
C(4)–C(5)–C(6)	119.2 (1.4)	C(15)–C(14)–C(13)	119.6 (1.4)
C(5)–C(6)–C(7)	118.8 (1.4)	C(14)–C(13)–C(12)	120.1 (1.2)
C(6)–C(7)–C(8)	121.2 (1.2)	C(13)–C(12)–C(11)	119.8 (1.1)
C(7)–C(8)–C(3)	118.8 (1.2)	C(12)–C(11)–C(16)	121.2 (1.2)
C(8)–C(3)–C(4)	118.6 (1.2)	C(11)–C(16)–C(15)	118.0 (1.2)
C(7)–C(8)–C(9)	119.3 (1.2)	C(12)–C(11)–C(10)	118.7 (1.1)
C(3)–C(8)–C(9)	121.7 (1.2)	C(16)–C(11)–C(10)	119.8 (1.2)
C(8)–C(9)–O(3)	122.0 (1.2)	C(11)–C(10)–O(6)	124.7 (1.2)
C(8)–C(9)–O(4)	112.6 (1.2)	C(11)–C(10)–O(5)	113.4 (1.2)
O(3)–C(9)–O(4)	124.9 (1.2)	O(5)–C(10)–O(6)	119.3 (1.2)

(Gupta & Sahu, 1971; Gupta & Dubey, 1972). As Table 2 shows, in both the homophthalic acid residues only one of the two carboxyl groups is ionized. The correct formula of the organic residue is, therefore, $C_9H_7O_4$. Also, as reported earlier (Gupta & Sahu, 1971; Gupta & Dubey, 1972), one of the carboxyl groups in each organic residue is nearly at right angles to the central aromatic ring (Table 3) while the other is rotated out of this plane by 12.2 and 11.7°. Other

dimensions of the two independent organic residues are normal and similar.

(b) Coordination polyhedra around the calcium ion

The Ca ion is surrounded by eight O atoms (Table 4) with an average Ca–O distance of 2.48 Å. The coordination polyhedron is a distorted antiprism. Moreover two such adjacent polyhedra share an edge, formed by $W(1)–W(1')$ (Fig. 1). This results in a deformation of the polyhedra and increased cation–anion distance (2.51 to 2.70 Å).

Table 4. Ca–O ionic distances (Å) and O–Ca–O angles (°)

Symmetry code			
(i)	$-x$	$-y$	$-z$
(ii) $\frac{1}{2}$	x	$y-1$	z
(iii)	x	y	$z-1$
(iv)	$-x$	$-y$	$1-z$

Ca– $W(4^{iv})$	2.36	Ca– $W(5^{iv})$	2.46
Ca– $W(3^{ii})$	2.39	Ca– $W(1)$	2.51
Ca–O(1)	2.40	Ca–O(2)	2.68
Ca– $W(2)$	2.40	Ca– $W(1')$	2.70
$W(4^{iv})$ –Ca– $W(3^{ii})$	78.4	O(1)–Ca– $W(5^{iv})$	72.6
$W(4^{iv})$ –Ca– $W(2)$	79.6	O(1)–Ca– $W(1)$	80.1
$W(4^{iv})$ –Ca– $W(5^{iv})$	77.4	O(1)–Ca–O(2)	50.4
$W(4^{iv})$ –Ca– $W(1')$	75.5	$W(2)$ –Ca– $W(1)$	80.6
$W(3^{ii})$ –Ca– $W(2)$	79.9	$W(2)$ –Ca–O(2)	79.8
$W(3^{ii})$ –Ca– $W(5^{iv})$	74.1	$W(5^{iv})$ –Ca– $W(1')$	73.7
$W(3^{ii})$ –Ca–O(2)	79.4	$W(1)$ –Ca–O(2)	77.2
		$W(1)$ –Ca– $W(1')$	65.9

Table 5. Intermolecular contacts up to 3.20 Å

$W(1)–W(1')$	2.84	$W(4)–O(3^{iv})$	3.14
$W(1)–W(5^{iii})$	3.10	$W(5)–O(1^{iv})$	2.87
$W(1)–W(4^{iii})$	3.11	$W(5)–W(3^v)$	2.92
$W(1)–O(1)$	3.16	$W(5)–W(2^v)$	2.99
$W(1)–W(2)$	3.18	$W(5)–W(4)$	3.01
$W(2)–W(4^{iv})$	3.05	O(3)–O(8 ⁱⁱⁱ)	3.18
$W(3)–W(4^v)$	3.01	O(5)–C(3)	3.18

Table 3. Least-squares planes and deviations of atoms from the planes

(a) Equations of planes

	Equation	Plane
C(1), O(1) and O(2)	$0.1275x + 0.6963y - 0.7419z = -2.0632$	A
C(3) to C(8)	$-0.5315x + 0.5737y + 0.7474z = -2.2280$	B
C(9), O(3) and O(4)	$-0.4021x + 0.7381y + 0.6275z = -1.4365$	C
C(18), O(7) and O(8)	$-0.0658x + 0.6156y + 0.7296z = 7.1494$	D
C(11) to C(16)	$0.4457x + 0.5337y - 0.7855z = -0.8698$	E
C(10), O(5) and O(6)	$0.3347x + 0.6658y - 0.7124z = 0.8364$	F

Dihedral angles

A and B	101.7°	C and B	12.2°
D and E	105.4	F and E	11.7

(b) Deviations of the atoms from the planes

Plane B		Plane E	
C(3)	0.009 Å	C(7)	-0.002 Å
C(4)	-0.015	C(8)	-0.001
C(5)	0.011	C(9)*	0.046
C(6)	0.003	C(2)*	-0.157
		C(11)	0.012 Å
		C(12)	-0.006
		C(13)	0.003
		C(14)	-0.007
		C(15)	0.013 Å
		C(16)	-0.015
		C(10)*	-0.016
		C(17)*	0.015

* Atoms given zero weight in least-squares calculation.

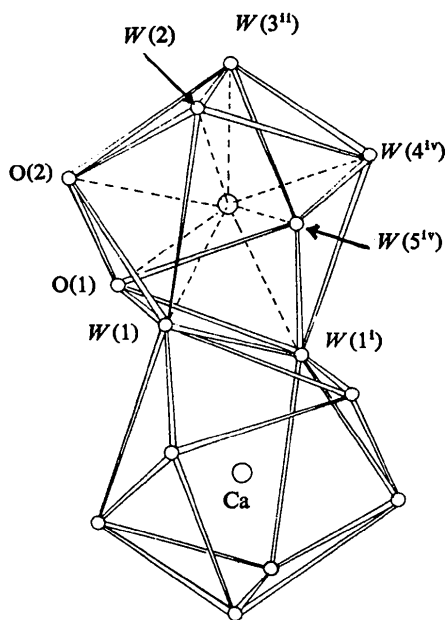


Fig. 1. Metal-oxygen polyhedra.

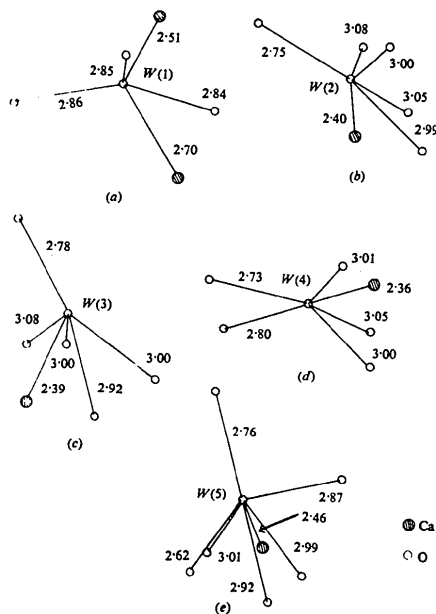


Fig. 2. Environments of the water molecules.

Table 6. *Hydrogen-bond parameters*

Donor (D)	Acceptor I [A(I)]	Acceptor II [A(II)]	D-A(I)	D-A(II)	$\angle A(I)-D-A(II)$
W(1)	O(1 ^v)	O(3)	2.85 Å	2.86 Å	106.7°
W(2)	W(3)	O(6)	3.00	2.75	90.0
W(3)	W(2 ^v)	O(7)	3.08	2.78	111.1
W(4)	O(7 ^{II})	O(8)	2.80	2.73	108.4
W(5)	O(7)	O(1 ^{vII})	2.62	2.76	114.4
O(4)	O(8 ^{III})		2.60	$\angle C(9)-O(4)-O(8III)$	108.2
O(5)	O(2)		2.59	$\angle C(10)-O(5)-O(2)$	113.5

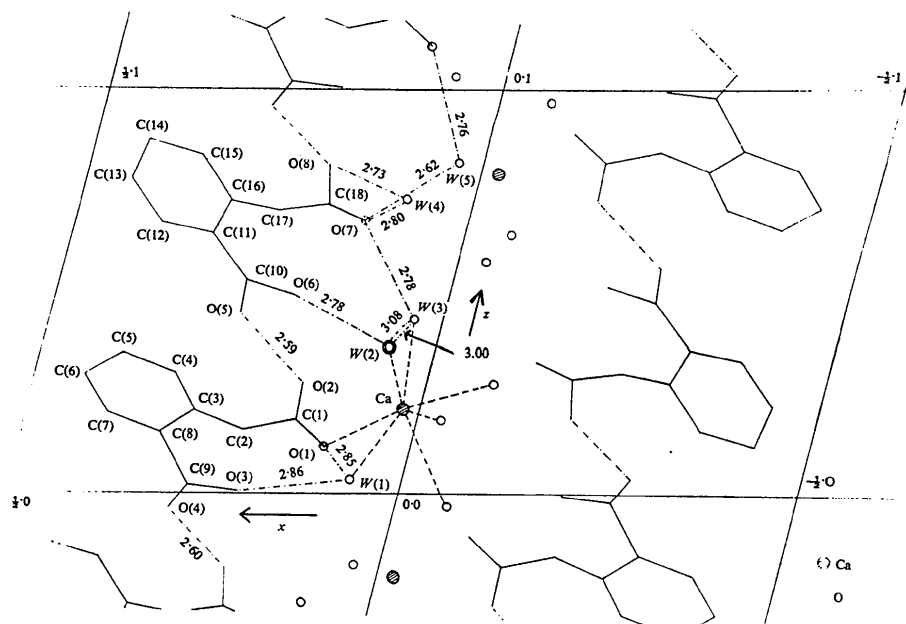


Fig. 3. Crystal structure viewed down [010].

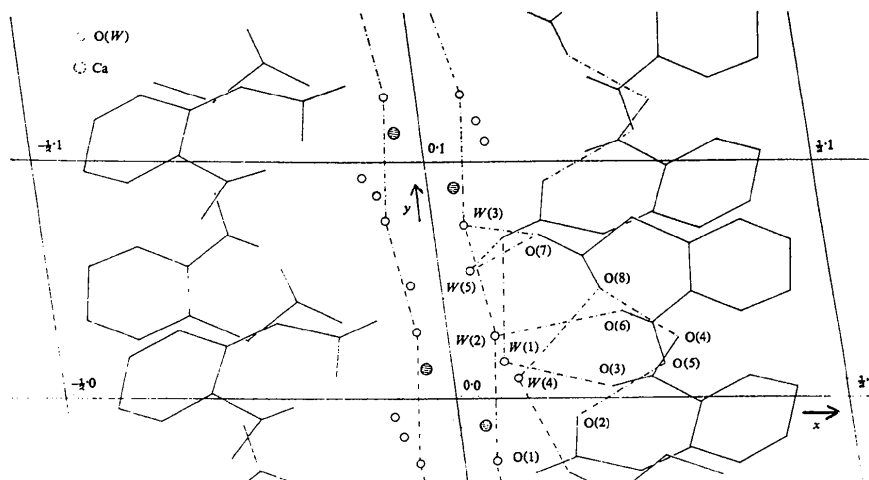


Fig. 4. Crystal structure viewed down [001].

(c) Environments of the water molecules

The environments of the five water molecules are shown in Fig. 2(a) to (e). Contact distances up to 3.10 Å have been assumed as likely distances for hydrogen bonds. $W(1)$, $W(2)$, $W(3)$, $W(4)$ and $W(5)$ conform to types *B*, *H*, *H*, *D* and *J* respectively in the notation of Ferraris & Franchini-Angela (1972).

Discussion of the structure

Figs. 3 and 4 show views of the structure down [010] and [001] respectively. The linkages are of the following types: (i) metal–oxygen ionic linkages (Table 4), (ii) hydrogen bonds (Table 6) between adjacent homophthalic acid residues through their carboxyl O atoms, (iii) hydrogen bonds *via* the five water molecules (Table 6) and (iv) van der Waals contacts.

In the crystal, adjacent homophthalic acid species are linked to each other through O atoms of their carboxyl groups, the un-ionized carboxyl group of one donating the proton to the other and so on, sequentially parallel to [001], in a herring-bone pattern (hydrogen bonds being 2.59 and 2.60 Å). The adjacent homophthalic acid species are, however, at different levels (viewed from [010]) and have opposite slants for their central aromatic rings. Located roughly at distances of $\frac{1}{3}a$ and $-\frac{1}{3}a$ from the origin, the two arrays of or-

ganic residues provide a broad 'separation channel' (Fig. 3) between which are packed all the Ca ions and water molecules.

$W(2)$ and $W(3)$ provide a vertical zigzag ascending column of hydrogen bonds (3.00 and 3.08 Å) parallel to [010] (Fig. 4). To this ascending column, other homophthalic acid residues are further linked by hydrogen bonds *via* $W(3)$ [$W(3)$ –O(7), 2.78 Å] and $W(2)$ [$W(2)$ –O(6), 2.75 Å]. This provides an extension of the network of hydrogen bonds in the [010] direction.

The two arrays of organic residues, located roughly at $\frac{1}{3}a$ and $\frac{2}{3}a$ from the origin are, however, linked by only weak van der Waals forces (Fig. 3).

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