Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

C(1)–P(1)	1·788 (7)	C(21)–P(1)–C(1)	110·9 (3)
C(21)–P(1)	1·791 (7)	C(31)–P(1)–C(1)	108·7 (3)
C(31)–P(1)	1·785 (8)	C(31)–P(1)–C(21)	107·5 (4)
C(41)–P(1)	1·776 (8)	C(41)–P(1)–C(1)	110·1 (3)
C(11)–O(1)	1·01 (2)	C(41)–P(1)–C(21)	109·5 (3)
		C(41)–P(1)–C(31)	110·1 (4)

Discussion. The three phenyl rings and the aliphatic chain are tetrahedrally disposed about the phosphorus ion, the rings being orientated to reduce steric interaction (Fig. 1). The rings are all planar and the aliphatic
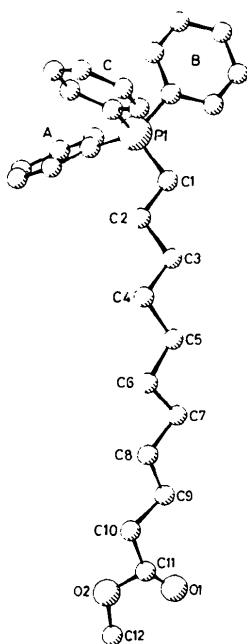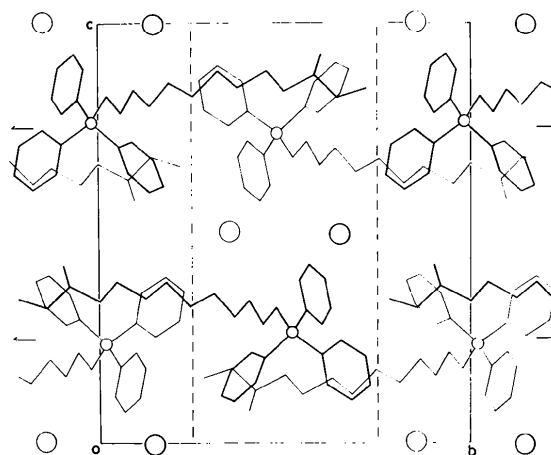

Fig. 1. A perspective view of the phosphonium cation.

Fig. 2. A projection of the structure viewed down a*.

chain is totally extended in a wide open curve. The iodide anions lie in spaces between the phosphonium cations, the packing being relatively loose (Fig. 2). There are no intermolecular or interionic close contacts.

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The Hydrogen Bonding of Artinite

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Abstract. $Mg_2CO_3(OH)_2(H_2O)_3$ (Utonai, Hokkaido, Japan), monoclinic, $C2/m$, $a = 16 \cdot 560$ (5), $b = 3 \cdot 153$ (1), $c = 6 \cdot 231$ (3) Å, $\beta = 99 \cdot 10$ (4)°, $Z = 2$, D_m (flotation) $= 2 \cdot 03$, $D_x = 2 \cdot 03$ g cm^{-3}. The H positions have been determined from three-dimensional X-ray data. The water molecules are hydrogen-bonded to O atoms of the carbonate groups and to those of the hydroxyl groups.

Introduction. Intensities were collected from an acicular crystal of dimensions $0.37 \times 0.10 \times 0.07$ mm with a Philips automated four-circle diffractometer and Mo $K\alpha$ radiation monochromated by a graphite plate. The ω–2θ scan technique was employed with a scan speed of $4°$ min^{-1} in ω. 640 independent reflexion data were obtained for $2\theta \leq 100°$. Intensities were corrected for Lorentz and polarization factors but not for extinction. No corrections were made for absorption, since μR of the crystal was less than 0.1 [μ(Mo $K\alpha = 5.0$ cm^{-1}]. The systematic absences, hkl for $h + k$ odd, are compatible with space group $C2/m$.

F_o was compared with F_c calculated from the atomic coordinates given by de Wolff (1952) and from those of Jagodzinski (1965); the R values were 0.42 and 0.38 respectively. At this point, a three-dimensional Patterson function was calculated and the Mg, O, and C

atoms were again located. The structure without H atoms was refined to an R value of 0.059. The positions of the H atoms were found from a difference Fourier synthesis. The structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) to a conventional R value of 0.049, employing anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The weighting scheme employed for the last cycles was $w = (28.7 - 3.01|F_o| + 0.101|F_o|^2 - 0.00085|F_o|^3)^{-1}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for the heavy atoms; for H those of Stewart, Davidson & Simpson (1965) were used. Final atomic parameters are given in Table 1.* Selected interatomic distances and bond angles are given in Table 2.

Discussion. Oscillation photographs of artinite exhibit very weak diffuse layer-lines with $k = $ odd/2, which are completely smeared into streaks. The diffuse layer-lines resemble those of $Na_2H_2P_4O_{12}$ owing to two-dimensional disorder (Gryder, Donnay & Ondik, 1958). An averaged structure of artinite was determined by de Wolff (1952) and refined by Jagodzinski (1965). However, no description has been reported to date for the H positions. The (010) projection of the previous structures is consistent with that of the present structure, although the previous ones are inadequate for a three-dimensional description. The x and z coordinates of the non-hydrogen atoms are close to those of Jagodzinski (1965), but the y coordinates are quite different from the previous values. In the previous

Table 1. *Final atomic parameters in artinite*

	x	y	z
Mg	0.31587 (6)	0.0	0.15203 (16)
O(H)	0.23884 (10)	0.5	0.17079 (29)
O(W)	0.39988 (11)	0.5	0.08992 (32)
O(1)	0.36702 (14)	0.0	0.46852 (35)
O(2)*	0.45155 (14)	0.35820 (93)	0.70358 (38)
C*	0.42330 (29)	0.0	0.62026 (74)

	x	y	z	B (Å^2)
H(1)	0.222 (3)	0.5	0.275 (7)	3.5 (9)
H(2)	0.443 (2)	0.5	0.174 (6)	2.7 (8)
H(3)	0.408 (3)	0.5	−0.039 (8)	3.3 (9)
H(4)*	0.395 (4)	0.195 (24)	0.528 (11)	5.7 (18)

* Site populations for O(2), C, and H(4) are all 0.5.

Table 2. *Interatomic distances (Å) and bond angles (°)*

Symmetry code

None	x,y,z	(iv)	$x, 1-y, z$
(i)	$x,\bar{y},z$	(v)	$\frac{1}{2}-x, \frac{1}{2}+y, 1-z$
(ii)	$1-x, y, 1-z$	(vi)	$\frac{1}{2}-x, \frac{1}{2}+y, z$
(iii)	$x, y, -1+z$		

MgO$_6$ octahedron

Mg–O(H)	2.043 (1) (×2)
Mg–O(H^{vi})	2.072 (2)
Mg–O(W)	2.177 (2) (×2)
Mg–O(1)	2.019 (2)

Carbonate group

C–O(1)	1.218 (5)
C–O(2)	1.299 (3) (×2)
O(1)–C–O(2)	119.6 (2)
O(2)–C–O(2^i)	120.8 (4)

Hydrogen bonds

	O–H	H···O	O···O	H–O–H
O(H)–H(1)···O(1^v)	0.75 (5)	2.35 (5)	3.061 (3)	163 (4)
O(W)–H(2)···O(2^{ii})	0.82 (4)	1.85 (4)	2.628 (3)	160 (3)
O(W)–H(3)···O(2^{iii})	0.83 (5)	1.92 (5)	2.716 (3)	161 (3)
O(1)–H(4)···O(2^{iv})	0.83 (7)	1.93 (7)	2.748 (3)	171 (7)

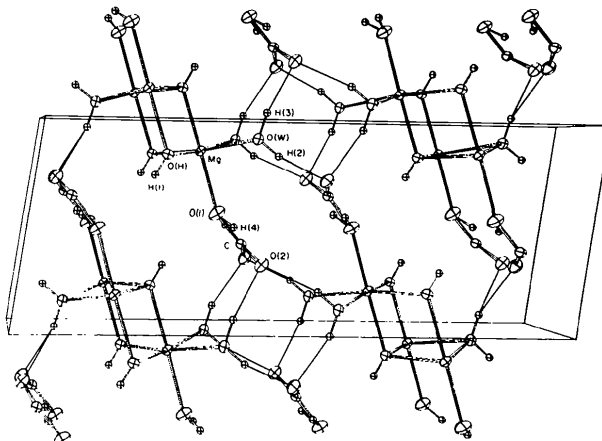| H(2)–O(W)–H(3) | 112 (4) |
| H(4)–O(1)–H(4^i) | 97 (7) |

Fig. 1. The crystal structure of artinite viewed along **b** (*ORTEP*, Johnson, 1965). Site populations for O(2), C, and H(4) are all 0.5.
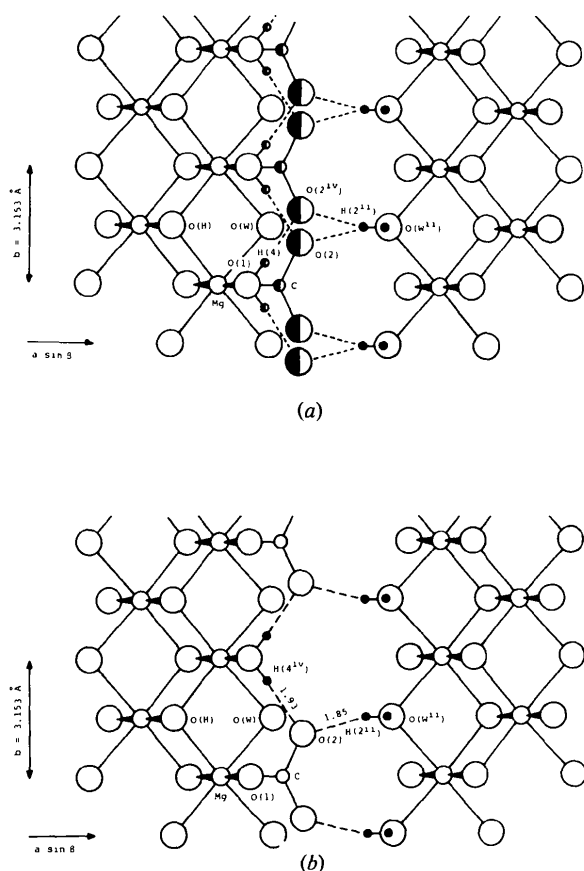
(a)

(b)

Fig. 2. Hydrogen-bonding scheme between carbonate groups and water molecules projected along c: (a) in the averaged structure, (b) in the actual structure. Hydrogen bonds are marked with dashed lines; half atoms are indicated by half-shaded circles.

structures $O(2^i)$ was mistaken for an independent atom because of wrong choices of origins.

Fig. 1 shows the structure viewed along **b**. The Mg atom is octahedrally surrounded by three hydroxyl groups, two water molecules, and one $O(1)$ atom. Half of the $O(1)$ atoms are O atoms of carbonate groups and the other half are from water molecules, since the occupancy factors for the $O(2)$, C, and $H(4)$ atoms are all 0.5.

The carbonate groups and the $O(1)$ water molecules alternate statistically along **b**. The MgO_6 octahedra are arranged in infinite chains parallel to **b** by sharing edges. The chains are cross-linked by hydrogen bonds between the carbonate groups and the $O(W)$ water molecules.

In Fig. 2 the hydrogen bonding between the carbonate groups and water molecules is shown schematically. In the averaged structure (Fig. 2a) it is possible that $H(2^{ii})$ of an $O(W)$ water molecule is hydrogen-bonded to $O(2)$ or $O(2^{iv})$ of a carbonate group; in both cases the hydrogen-bond distances are equal. The $O(2)–O(2^{iv})$ distance (0.894 Å) between the

neighbouring carbonate groups is shorter than the van der Waals radius of an O atom (1.40 Å). In the actual structure (Fig. 2b) the carbonate groups and the $O(1)$ water molecules which are attached to a chain of MgO_6 octahedra should strictly alternate along **b** with a true periodicity of $2b$. Every chain has two possible positions differing by a displacement of **b**, thus producing the two-dimensional disorder observed.

If $O(1)$ is the O atom of a water molecule, it is tetrahedrally surrounded by two $H(4)$, one Mg, and one $H(1)$ of a neighbouring hydroxyl group which acts as a donor of a hydrogen bond. If $O(1)$ is from a carbonate group, it has 'trigonal' planar coordination; the $C^v–O(1^v)\cdots H(1)$ angle ($88°$) is much smaller than the ideal value of $120°$.

The $O(W)$ and $O(1)$ water molecules are hydrogen-bonded to $O(2)$ atoms of the carbonate groups. The $O(2)$ atom is tetrahedrally surrounded by C, $H(2)$, $H(3)$, and $H(4)$ of neighbouring water molecules which act as donors of hydrogen bonds. The hydrogen bonds between $O(W)$ and $O(2)$ form a small quadrangle of dimensions 2.63×2.72 Å, as shown in Fig. 1.

The infrared spectrum of artinite reported by White (1971) shows a sharp band of almost free OH^- stretching vibration at 3610 cm^{-1} and two broad intense bands of strong hydrogen bonds at 3230 and 3020 cm^{-1}. In fact, there are three kinds of hydrogen bonds in the structure. (1) The very short $O(W)\cdots O(2^{ii})$ distance (2.628 Å) indicates the existence of a very strong hydrogen bond between these atoms. (2) The slightly longer $O(W)\cdots O(2^{iii})$ and $O(1)\cdots O(2^{iv})$ distances (2.716 and 2.748 Å respectively) indicate fairly strong hydrogen bonds. (3) The $O(H)$ hydroxyl group shows a very long (3.061 Å) $O\cdots O$ contact with $O(1^v)$, and this probably lies at the boundary of a very weak hydrogen bond.

We are grateful to Professor Y. Iitaka for his permission to use an automated diffractometer in his laboratory at the University of Tokyo. Computations were carried out on HITAC 8700 and M-180 computers at the Computer Centre of the Tokyo Institute of Technology.

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