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The Crystal Structure of Hydrated Gallium Phosphate of Composition $GaPO_4.2H_2O$

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The crystal structure of a hydrate of gallium phosphate, of composition $GaPO_4 . 2H_2O$, has been determined by means of X-ray diffraction. The structure was deduced from two- and three-dimensional Fourier and Patterson analyses, and refined by least squares to an R index of 0·074, with hydrogen positions neglected.

The monoclinic cell has dimensions, $a=9·77$, $b=9·64$, $c=9·68$ Å; $\beta=102·7°$. The space group is $P2_1/n$ (C_{2h}^5). For a cell containing four units of $(GaPO_4)_2 . 4H_2O$, the calculated density is 3·00 g.cm^{-3}. With hydrogen positions assumed, the crystal may be described structurally as $[Ga_2(OH)(H_4O_2)](H_2O)(H)(PO_4)_2$. The atoms within the square brackets are interconnected so as to form an infinite double chain complex. Such chains connect surrounding phosphate groups, through gallium and 'water-oxygen' bonds, into a channelled, three-dimensional network. The channels contain an additional 'water-oxygen' atom, environed only by six phosphate oxygen atoms somewhat irregularly distributed about it. It is assumed to be an $H . H_2O$ complex in a disordered state.

Both gallium atoms have a coordination of six; namely, four phosphate oxygen and two 'water-oxygen' atoms. The average gallium to oxygen coordination distance is 1·99 Å. However, four gallium coordination octahedra are interconnected by two 'water-oxygen' atoms, which form an edge common to two and a pair of corners common to three octahedra. In consequence of the shared edge, pairs of gallium atoms are separated by a distance of 3·06 Å. All other gallium–gallium distances are at least 3·75 Å.

Introduction

Previous studies have shown that anhydrous gallium phosphate, $GaPO_4$, is isostructural with $AlPO_4$, a low quartz analogue; and that like $AlPO_4$ it has high temperature phases closely to the cristobalite and high cristobalite silica structures (Mooney, Kissinger & Perloff, 1954; Perloff, 1954; Mooney, 1956). Though a number of hydrated forms of aluminum phosphate exist, particularly among minerals, only one hydrated phosphate of gallium, a trihydrate, has been reported in the literature (Neogi & Nandi, 1936.)

An interest in the crystal chemistry of gallium, as well as in the function of water in the insoluble hydrated phosphates, prompted the undertaking of a structure analysis of the compound. However, our attempt to prepare suitable crystals of hydrated gallium phosphate produced, not the trihydrate, but excellent crystals of composition $GaPO_4 . 2H_2O$. The structure of these crystals, derived from X-ray analysis, is the subject of the present report. As may be expected in the case of a highly insoluble hydrate such as this, the simple formula derived from chemical analysis does not properly describe the nature of the water content in the solid.

Preparation of the crystals

Neogi & Nandi precipitated gallium phosphate trihydrate by adding acid sodium phosphate to a slightly acidified solution of gallium nitrate. The product, an initially amorphous powder, became crystalline after long digestion. For our purposes, larger crystals were required. They were obtained by a method for the preparation of water-insoluble phosphates originally devised by de Schulten (1903); that is, by the very slow dilution or neutralization of an acid solution of the phosphate held at a moderately elevated temperatures. The crystals of hydrated gallium phosphate which were grown in this way were clear, well formed monoclinic prisms, the largest of which had linear dimensions close to 0·16 × 0·25 × 0·40 mm. Their hydration, however, proved to be different from that of Neogi & Nandi's compound.

The water content of air dried crystals was assessed by heating a small sample, in stages, to constant weight. The total weight loss was equivalent to $2H_2O$ per $GaPO_4$. The water loss began between 100°C and 110 °C, and continued, with fluctuations, up to about 370 °C. After this heat treatment, the sample was found to be amorphous.

Experimental procedure

A Nonius integrating Weissenberg spectrometer was used for the collection of diffraction data. Patterns were taken of all available layers about each of the crystal axes, and recorded on triple film packs with nickel filtered copper radiation. The integrated intensities were evaluated by means of a simple spot densitometer, and converted to F^2 values by application of the polarization and Lorentz factors. The reflections were placed on a common arbitrary scale by correlation of data from different films, and eventually scaled to correspond to calculated F values.

The Patterson and Fourier distributions were calculated by means of Sly, Shoemaker & van den Hende's (1962) program for the IBM 7090 computer. The least-square refinements were done with the Busing & Levy (1959) full-matrix program adapted to the IBM 709 computer.

The atomic scattering factors required for structure amplitude calculations were taken from the *International Tables for X-ray Crystallography* (1962), Table 3.3.1 A.

Crystal data

Gallium phosphate dihydrate crystallizes in the monoclinic system. The cell, measured from rotation and Weissenberg diagrams with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}540$ Å) has the following dimensions: $a = 9{\cdot}77 \pm 0{\cdot}01$, $b = 9{\cdot}64 \pm 0{\cdot}01$, $c = 9{\cdot}68 \pm 0{\cdot}01$ Å; $\beta = 102{\cdot}7° \pm 0{\cdot}2°$. The density, estimated by flotation, appeared to be greater than 2·8 g.cm^{-3} and less than 3·2 g.cm^{-3}. The calculated density, on the basis of eight formula weights of $GaPO_4 . 2H_2O$ per unit cell, is 2·998 g.cm^{-3}.

There are no systematic absences among reflections hkl, but reflections $0k0$ are absent unless $k = 2n$, and reflections $h0l$ are absent unless $h + l = 2n$. On this evidence, the space group was taken as $P2_1/n$ (C_{2h}^5). The general positions prescribed by the space group are fourfold. It follows that, if all of the atoms occupy general positions, the asymmetric structure unit is $Ga_2(PO_4)_2 . 4H_2O$. In other words, the crystal is built up of two geometrically unequivalent sets of gallium and of phosphate groups and four geometrically and possibly chemically different sets of 'water oxygen atoms'.

In order to facilitate tabulation and discussions, the twelve oxygen atoms of the asymmetric unit are specified as follows. The phosphate group oxygen atoms which are associated with P(1) are numbered from O(1) to O(4), and those associated with P(2) are numbered from O(5) to O(8). The remaining four oxygen atoms, which are known to be expelled as H_2O under prolonged heat treatment but do not necessarily exist as H_2O groups in the solid, are nevertheless referred to as water oxygen atoms, and are tagged as O(w1) to O(w4). These symbols are used in abbreviated form – for example, w(1) – in the discussions.

Determination of the approximate structure

The entire set of experimental F^2 values, consisting of 1022 independent observations, was synthesized into a three-dimensional Patterson summation. In the resulting set of contoured graphs, the most prominent feature was the peak systems due to Ga(1)–Ga(1), Ga(2)–Ga(2), and Ga(1)–Ga(2) vectors. An analysis of this collection of peak positions yielded tentative parameters for the two sets of gallium atoms. Use was made of these parameters in locating three of the light atoms, largely by means of their gallium interaction peaks. The F values calculated from this structure fragment gave promising agreement with the general run of observations. Therefore, their signs were used to phase the observed F values for a three-dimensional Fourier synthesis.

The electron density maps resulting from this first trial were somewhat crude, but led to the identification of the phosphorus atoms, with their surrounding clusters of oxygen, and also of one w-oxygen atom. The F values calculated from the augmented structure showed changes in about 12% of the signs. A second three-dimensional Fourier synthesis, calculated with a corrected set of signs, gave approximate positions for all of the atoms in the cell, hydrogen excepted.

As a rough check of the approximate structure, and for a first scaling to absolute values, the entire set of F values was entered into a least-squares calculation, in which one scale factor, an overall temperature factor, and uniform weighing were used. All of the parameters were allowed to vary. All underwent readjustments, and the R index, originally 52%, fell to 30% in four cycles. The structure established by the trial parameters seemed chemically reasonable, and its refinement was undertaken.

The refinement

The refinement was effected by means of a series of least-squares calculations in which a separate scale factor was used for each level, and an isotropic temperature factor for each atom. The weighing scheme employed was that originally proposed by Hughes (1941) for photographic data. Initially, the entire set of data was entered into the calculations, which, after corrections based on Fourier difference results, converged on a residual value of 0·13. The correlation between parameters was entirely negligible, but it was obvious, from the systematic nature of some larger discrepancies between F_o and F_c, that the absorption of the crystal could not be ignored. Therefore, the $hk0$, $h0l$ and $0kl$ zones were corrected for absorption by a graphical method (Rogers & Moffat, 1956) and this reduced set of data, consisting of 341 observations, 238 measurable, was used in a final refinement of the parameters.

Small changes in the temperature factors of the lighter atoms occurred, but there were no alterations in the positional parameters of any significance. The final difference Fourier maps, in this case a set of three two-dimensional projections, were featureless. No indications of the possible locations of the hydrogen atoms were obtained at any stage, and no assumptions concerning hydrogen positions were used in any of the calculations.

The terminal R value for the reduced set of data is 0·074 for observed F values, and 0·134 if unobserved F values are included with zero values. The unobserved reflections, without exception, have calculated F values below the observational limit, but their number is large. The structural parameters, with standard deviations obtained from the least squares program, are given in Table 1. A comparison of observed and calculated F values appears in Table 2.

Description of the structure

Both Ga(1) and Ga(2) are octahedrally coordinated. Each is bound to two water-oxygen atoms and to four phosphate oxygens, the corners of different phosphate tetrahedra. However, four gallium coordination octahedra (Fig. 1) are interconnected in the following way. Two Ga(1) octahedra share an edge, a pair of *w*(1) oxygen atoms and each *w*(1) is also the corner of a Ga(2) octahedron, thus being held in common by three gallium atoms. If one wishes to describe the structure in terms of packed polyhedra, the complex of four gallium–oxygen octahedra may be thought of as a structural unit. Such units, linked together by pairs of *w*(3) oxygen atoms, and interconnected by tetrahedrally coordinated phosphorus atoms, build up a continuous, channelled network. The channels extend roughly in the *b*-axial direction and contain *w*(4) oxygen atoms.

From a chemical point of view, it is of interest to describe the structure in a slightly different fashion. Both gallium atoms, and three of the four water oxygen atoms, that is *w*(1), *w*(2) and *w*(3), are associated so as to build up an infinite double chain, which represents the principal cationic component of the crystal. The configuration (see Fig. 3) may be described as a succession of nearly flat, four-cornered links, the planes of which are turned sharply with respect to each other. Within the chain, each *w*(1) is bound to three gallium atoms, namely, two Ga(1) and one Ga(2), while *w*(2) is bound to Ga(2). The *w*(3) oxygen atom has no gallium contact, but serves as a connecting link between *w*(1) and *w*(2) oxygen atoms of different gallium coordination groups. The chains zigzag through the crystal in the *b*-axial direction, and are connected to surrounding phosphate group oxygen atoms mainly by means of gallium, but also by *w*(2) and *w*(3) bonds. Oxygen *w*(1) forms no bonds external to the chain. The *w*(4) oxygen is too far removed from the chain system to have any connection with it, and is surrounded only by phosphate oxygens.

Fig. 2, a projection of the structure along the *b*-axial direction, shows something of the packing scheme of the crystal, with an end-on view of the water oxygen–gallium chain system and the channels containing *w*(4). The gross features of the arrangement lead to a preliminary structural formula, $Ga_2(O_w)_3(PO_4)_2 . O_w$, in which each O_w represents an oxygen atom with unspecified hydrogen association. The total number of oxygen atoms must be eight, but it does not necessarily follow that all four *w*-oxygen atoms are H_2O species.

Table 1. *Positional parameters* ($\times 10^4$) *and isotropic temperature factors* β, ($\times 10^2$) *with their calculated standard deviations*

	x/a	y/b	z/c	β
Ga(1)	1287 ± 2	4587 ± 3	1128 ± 3	59 ± 4
Ga(2)	3158 ± 2	2693 ± 2	6008 ± 2	48 ± 4
P(1)	1323 ± 5	1873 ± 6	2926 ± 5	75 ± 8
P(2)	1505 ± 5	4647 ± 6	7958 ± 5	61 ± 8
O(1)	1617 ± 11	2316 ± 12	4478 ± 11	136 ± 19
O(2)	2040 ± 12	2927 ± 14	2047 ± 13	196 ± 22
O(3)	9768 ± 13	1694 ± 12	2367 ± 13	130 ± 22
O(4)	1990 ± 14	0479 ± 17	2803 ± 15	133 ± 25
O(5)	9922 ± 14	4808 ± 14	7630 ± 13	128 ± 24
O(6)	2059 ± 12	4075 ± 14	9471 ± 14	151 ± 22
O(7)	1868 ± 11	3696 ± 14	6851 ± 11	150 ± 20
O(8)	2219 ± 15	6106 ± 17	7825 ± 13	155 ± 24
O(w1)	0525 ± 13	6453 ± 14	9959 ± 11	165 ± 19
O(w2)	3506 ± 12	4403 ± 13	4956 ± 12	165 ± 20
O(w3)	0369 ± 13	1370 ± 14	8210 ± 13	160 ± 21
O(w4)	3988 ± 13	1837 ± 13	0120 ± 12	192 ± 22

Table 2. *Observed and calculated F values*

h	0	l	F_o	F_c
0	0	2	80	-77
		4	*	14
		6	74	-70
		8	43	42
		10	138	135
		12	34	-40
1	0	1	140	143
		3	39	-35
		5	50	-46
		7	*	1
		9	*	29
		11	*	8
$\bar{1}$	0	1	104	107
		3	91	-92
		5	58	-56
		7	*	9
		9	114	118
		11	33	32
2	0	2	35	33
		4	39	39
		6	161	153
		8	*	-11
		10	58	57
$\bar{2}$	0	2	49	-49
		4	90	84
		6	80	-77
		8	74	73
		10	45	-43
$\bar{2}$	0	12	39	37
3	0	1	169	-176
		3	55	-56
		5	142	143
		7	36	45
		9	72	-74
		11	76	-77
$\bar{3}$	0	1	54	-55
		3	143	142
		5	163	159
		7	65	-64
		9	100	-93
		11	*	1
4	0	2	131	-136
		4	*	5
		6	*	9
		8	39	44
		10	81	-82
$\bar{4}$	0	2	29	26
		4	154	155
		6	*	-14
		8	108	-106
		10	74	-71
		12	61	65
5	0	1	97	98
		3	*	20
		5	*	13
		7	54	-51
5	0	9	51	49
$\bar{5}$	0	1	*	9
		3	23	-23
		5	*	12
		7	45	-42
		9	*	-1
		11	*	1
6	0	2	70	71
		4	56	56
		6	134	-137
		8	36	-31
$\bar{6}$	0	2	145	-148
		4	107	-115
		6	52	50
		8	33	38
		10	21	21
		12	56	-49
7	0	1	120	115
		3	48	45
		5	38	-38
		7	32	-30
$\bar{7}$	0	1	89	-86
		3	107	-113
		5	*	1
		7	87	94
		9	78	84
		11	57	-59
8	0	2	*	-15
8	0	4	21	-22
		6	31	33
$\bar{8}$	0	2	66	-65
		4	51	49
		6	34	-30
		8	55	-55
9	0	1	54	-57
		3	104	-99
		5	*	-9
$\bar{9}$	0	1	39	34
		3	100	98
		5	41	-43
		7	78	-79
		9	40	-36
10	0	2	63	-61
		4	73	-75
$\bar{10}$	0	2	80	77
		4	56	57
		6	126	-130
		8	28	-30
11	0	1	36	-38
		3	*	13
$\bar{11}$	0	1	20	13
		3	20	-17
		5	43	-46
		7	47	-48
$\bar{12}$	0	2	*	-50
		4	39	-35

Scale factor 0.495

0	k	l	F_o	F_c
0	1	1	100	-97
		2	99	-101
		3	103	98
		4	43	-46
		5	*	20
		6	91	91
		7	56	57
		8	64	64
		9	80	-77
		10	*	-18
		11	*	32
0	2	0		-13
		1	54	-53
		2	57	-53
		3	41	41
		4	*	9
		5	59	-59
		6	20	19
		7	20	-25
		8	33	33
		9	*	19
		10	*	-15
		11	*	3
0	3	1	75	-78
		2	35	36
		3	85	91
		4	*	13
		5	68	67
0	3	6	*	22
		7	*	2
		8	33	-36
		9	53	-50
		10	*	-16
		11	*	-15
0	4	0	104	109
		1	71	64
		2	21	16
		3	106	108
		4	95	-95
		5	*	-19
		6	94	-96
		7	84	-86
		8	39	40
		9	*	4
		10	55	55
		11	49	49
0	5	1	21	20
		2	120	-113
		3	62	62
		4	67	-67
		5	68	-69
		6	132	137
		7	23	25
		8	55	56
		9	*	-2
		10	*	-11
0	5	11	*	13
0	6	0	*	-14
		1	55	-54
		2	74	-73
		3	60	62
		4	73	73
		5	54	-52
		6	46	43
		7	27	-24
		8	*	-4
		9	39	36
		10	*	-9
0	7	1	25	-24
		2	*	2
		3	44	-42
		4	72	-69
		5	42	45
		6	59	66
		7	*	-26
		8	54	-51
		9	38	-39
		10	*	-10
0	8	0	*	-22
		1	*	13
		2	20	16
		3	150	153
		4	*	-30
		5	*	-28
0	8	6	*	-13
		7	64	-63
		8	*	-17
		9	*	-1
0	9	1	57	53
		2	55	-57
		3	65	-62
		4	41	-38
		5	74	-71
		6	49	51
		7	*	-9
		8	27	27
0	10	0	74	-69
		1	*	-11
		2	*	-19
		3	*	-26
		4	46	46
		5	*	-7
		6	*	12
		7	*	13
0	11	1	*	-3
		2	*	2
		3	*	9
		4	*	-9
		5	*	5
0	12	0	59	-57
		1	*	-4
		2	*	22

Scale factor 0.503

h	k	0	F_o	F_c
1	1	0	107	-107
	2		59	64
	3		114	-120
	4		81	81
	5		*	4
	6		110	109
	7		35	-31
	8		*	1
	9		20	32
	10		76	80
	11		25	22
	12		45	-41
2	0	0	127	-130
	1		23	-20
	2		48	49
	3		121	-131
	4		66	-66
	5		63	-63
	6		99	102
	7		122	125
	8		*	-13
	9		20	-31
	10		*	2
	11		50	-48
	12		*	17
3	1	0	88	87
	2		32	-30
	3		45	46
	4		129	135
3	5	0	62	-62
	6		40	36
	7		61	61
	8		61	58
	9		69	-68
	10		*	10
	11		*	-3
	12		*	7
4	0	0	122	-125
	1		*	0
	2		51	-51
	3		95	92
	4		88	-88
	5		41	-42
	6		*	-2
	7		77	78
	8		69	70
	9		*	-11
	10		42	43
	11		22	21
5	1	0	32	31
	2		81	-80
	3		21	15
	4		102	-107
	5		57	56
	6		60	-58
	7		46	-46
	8		60	-55
5	9	0	*	-10
	10		75	-73
	11		69	-69
6	0	0	157	161
	1		78	76
	2		21	-21
	3		*	-11
	4		88	89
	5		80	82
	6		29	-30
	7		63	64
	8		*	16
	9		49	48
	10		*	-33
7	1	0	55	-50
	2		*	23
	3		115	-122
	4		77	-79
	5		31	-25
	6		*	21
	7		*	-3
	8		65	-62
	9		*	20
	10		*	7
8	0	0	*	[illegible]
	1		*	12
	2		114	115
	3		*	-16
	4		*	2
8	5	0	*	-8
	6		66	64
	7		30	-22
	8		71	-72
	9		*	-21
9	1	0	20	-36
	2		*	-4
	3		*	-8
	4		99	98
	5		*	-18
	6		30	34
	7		34	37
	8		76	83
10	0	0	*	1
	1		62	60
	2		43	-43
	3		*	13
	4		*	9
	5		66	-66
	6		*	-22
11	1	0	37	36
	2		*	9
	3		40	36
	4		*	-11
	5		*	15
12	0	0	49	-50
	1		47	51
	2		21	-26

Scale factor 0.505

* unobserved

Interatomic distances

Interatomic distances are given in Table 3. The standard errors calculated from the least-squares program and averaged are 0·005 Å for Ga–Ga distances; 0·025 for Ga–O and P–O distances, and 0·030 for O–O distances.

The two phosphate groups are somewhat distorted tetrahedra with an average P–O distance of 1·54 Å. The individual values, 1·51 to 1·59 Å, are within the

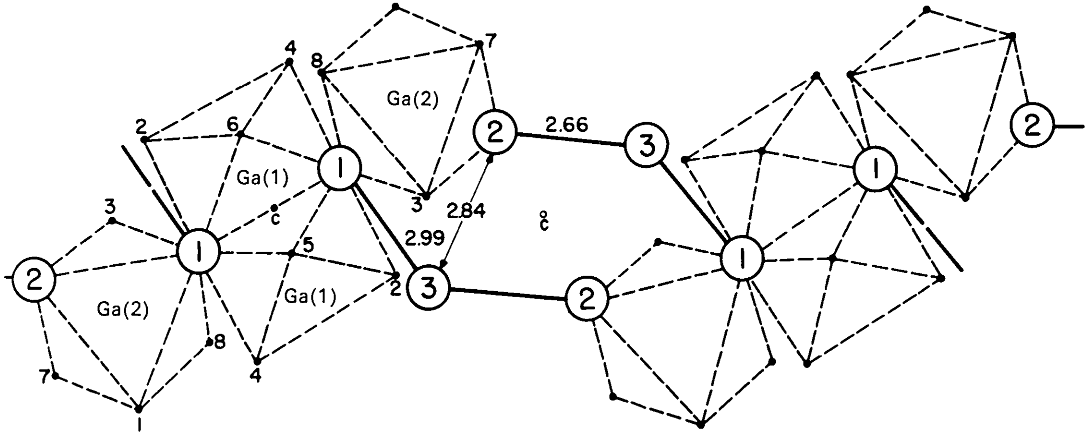

Fig. 1. The complex of gallium octahedra and their interconnection into an infinite chain. The *w*-oxygen atoms are represented by open circles and the phosphate oxygen atoms by dots at octahedron corners, appropriately numbered for identification. The additional bonds formed by *w*(2) and *w*(3) external to the chain are omitted for clarity.

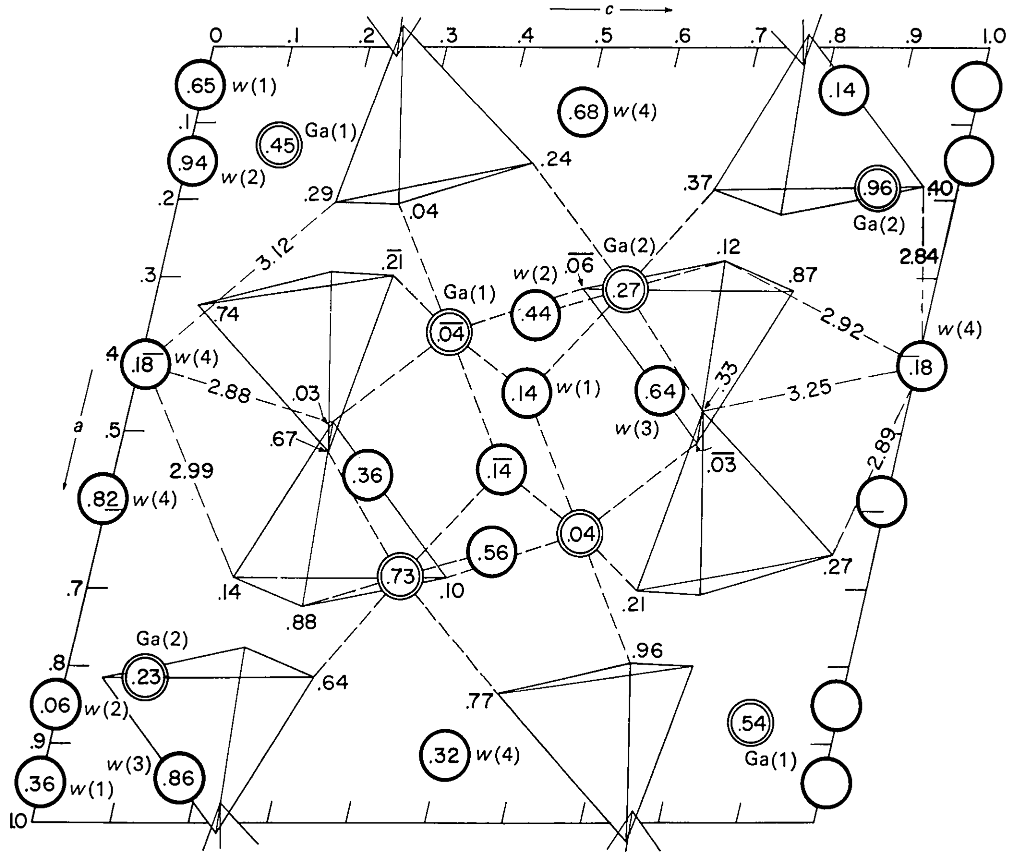

Fig. 2. Projection along the *b*-axial direction of one unit cell of the structure. Gallium and water-oxygen positions are shown by double and single rings respectively, and phosphate oxygen atoms are understood to occupy corners of the tetrahedral figures. The displacement of an atom in the **b** direction is given numerically as the fraction, y/b. The gallium and water-oxygen complex occupies the center of the diagram. The gallium coordination is indicated by dashed lines. The nearest neighbors of a *w*(4) at the edge of the diagram are also indicated.

range commonly found in phosphates (*International Tables for X-ray Crystallography*, 1962). Each phosphate oxygen atom is coordinated to one gallium atom at an average distance of 1·94 Å, and has one or two water-oxygen neighbors at distances between 2·77 and 3·20 Å. Except for close neighbors within the same gallium coordination octahedra, the shortest distances between oxygen atoms of different phosphate groups are 3·4 and 3·6 Å.

If no distinction is made between phosphate oxygen atoms and water oxygen atoms, the average gallium–oxygen distance for six coordination is found to be 1·99 Å. However, the average distances between gallium and phosphate oxygen atoms is 1·94 Å, while the average gallium to water–oxygen distance, 2·10 Å, may possibly be significantly larger. There seem to be no well established experimental values with which to compare these results. The sum of the empirical ionic radii (Pauling, 1960) is 2·02 Å. In anhydrous gallium phosphate (low cristobalite type), four-coordinated gallium has Ga–O distances of 1·78 Å (Mooney, 1956), considerably smaller than the value of about 1·85 Å which would be predicted from the sum of the ionic radii.

The sharing of edges between two Ga(1) octahedra results in the pairing of Ga(1) atoms at a distance of 3·06 Å. All other gallium distances are at least 3·75 Å. In the metal, (Sharma & Donohue, 1962) pairs of gallium atoms are separated by only 2·484 Å, and the distances to other nearest neighbors range between 2·69 Å and 2·79 Å.

Numerical data concerning the environment of each of the *w*-oxygen atoms are collected in Tables 3 and 4. In addition to neighbors within the chain as in the case of *w*(1), *w*(2) and *w*(3), there are various numbers of phosphate oxygen atoms within possible bonding distance of the *w*-oxygen atoms; none for *w*(1), but two for *w*(2), five for *w*(3) and six for *w*(4), at distances between 2·77 and 3·20 Å. All are not necessarily bonded to *w*-oxygen atoms; however, the detailed examina-

Table 3. *Interatomic distances and angles*

(*a*) The gallium octahedra

Ga(1)	–O(*w*1)	2·17 Å	Ga(2)	–O(*w*1)	2·12 Å
	O(*w*1′)	2·10		O(*w*2)	2·01
	O(2)	1·90		O(1)	1·90
	O(4)	1·97		O(3)	1·91
	O(5)	1·95		O(7)	1·91
	O(6)	1·98		O(8)	1·98
O(*w*1)	–O(*w*1′)	2·99	O(*w*1)	–O(*w*2)	2·99
	O(4)	3·03		O(1)	2·85
	O(5)	2·75		O(3)	2·84
	O(6)	2·83		O(8)	2·94
O(*w*1′)	–O(2)	2·88	O(*w*2)	–O(1)	2·70
	O(5)	2·71		O(3)	2·61
	O(6)	2·75		O(7)	2·77
O(2)	–O(4)	2·63	O(1)	–O(7)	2·62
	O(5)	2·97		O(8)	2·86
	O(6)	2·73	O(3)	–O(7)	2·79
O(4)	–O(5)	2·92		O(8)	2·85
	O(6)	2·93	O(7)	–O(8)	2·65
Av. ∢, 90·0 ± 4·6°			Av. ∢, 90·0 ± 2·9°		

(*b*) The phosphate groups

P(1)	–O(1)	1·53 Å	P(2)	–O(5)	1·52 Å
	O(2)	1·58		O(6)	1·55
	O(3)	1·51		O(7)	1·51
	O(4)	1·51		O(8)	1·59
O(1)	–O(2)	2·55	O(5)	–O(6)	2·53
	O(3)	2·48		O(7)	2·44
	O(4)	2·48		O(8)	2·54
O(2)	–O(3)	2·60	O(6)	O(7)	2·53
	O(4)	2·47		O(8)	2·55
O(3)	–O(4)	2·42	O(7)	–O(8)	2·50
Av. ∢ 109·45 ± 1·96°			Av. ∢ 109·46 ± 1·41°		

(*c*) Nearest neighbors, *w*-oxygen atoms to phosphate oxygen atoms

O(*w*1)	–O(*w*3)	2·99 Å	O(*w*2)	–O(4)	2·81 Å
O(*w*3)	–O(*w*2)	2·66		O(2)	3·20
	O(*w*2′)	2·84	O(*w*4)	–O(1)	2·89
	O(8)	2·77		O(5)	2·88
	O(4)	2·91		O(6)	2·84
	O(3)	3·00		O(8)	2·92
	O(7)	3·12		O(7)	2·99
	O(6)	3·18		O(2)	3·12

Table 4. *Angles involving atoms, A, C and B, where C, a water-oxygen atom, is at the apex*

Configurations are illustrated in Figs. 2 and 4, with notation following that of the table.

Atoms			Angles (°)	Distances (Å)		
A	*C*	*B*		*C–A*	*C–B*	*A–B*
Ga(1)	*w*(1)	Ga(1′)	91·1	2·17	2·11	3·05
Ga(1′)		Ga(2′)	125·1	2·11	2·12	3·74
Ga(2′)		Ga(1)	121·8	2·12	2·17	3·75
Ga(1)		*w*(3)	112·6	2·17	2·99	4·32
w(3)		Ga(1′)	107·8	2·99	2·11	4·16
Ga(2′)		*w*(3)	98·7	2·17	2·99	3·92
Ga(2)	*w*(2)	*w*(3)	109·8	2·01	2·66	3·84
w(3)		O(4)	109·3	2·66	2·81	4·46
O(4)		Ga(2)	140·8	2·81	2·01	4·54
w(3′)		Ga(2)	106·8	2·84	2·01	3·92
w(3′)		*w*(3)	111·0	2·84	2·66	4·54
w(3′)		O(4)	62·0	2·84	2·81	2·91
w(2)	*w*(3)	*w*(1)	103·6	2·66	2·99	4·46
w(1)		O(4)	108·4	2·99	2·91	4·79
O(4)		*w*(2)	88·0	2·91	2·66	3·88
w(2)		O(8)	85·0	2·66	2·77	3·68
O(8)		*w*(1)	131·3	2·77	2·99	5·25
O(4)		O(8)	119·8	2·91	2·77	4·91
w(2′)		*w*(1)	61·6	2·84	2·99	2·99
w(2′)		*w*(2)	69·0	2·84	2·66	3·12
w(2′)		O(8)	154·0	2·84	2·77	5·47
w(2′)		O(4)	58·0	2·84	2·91	2·81
O(5)	*w*(4)	O(1)	101·8	2·88	2·89	4·48
O(1)		O(6)	108·4	2·89	2·84	4·65
O(6)		O(5)	132·6	2·84	2·88	5·24
O(7)		O(2)	110·3	2·99	3·12	5·01
O(2)		O(8)	119·8	3·12	2·92	5·26
O(8)		O(7)	129·4	2·92	2·99	5·34
O(1)		O(8)	92·6	2·89	2·92	4·20
O(5)		O(8)	132·5	2·88	2·92	5·31
O(6)		O(8)	82·1	2·84	2·92	3·78
O(1)		O(7)	52·9	2·89	2·99	2·62†
O(5)		O(7)	49·2	2·88	2·99	2·44*
O(6)		O(7)	138·8	2·84	2·99	5·46
O(1)		O(2)	136·1	2·89	3·12	5·57
O(5)		O(2)	80·5	2·88	3·12	3·81
O(6)		O(2)	54·2	2·84	3·12	2·73†

* Tetrahedron edge.

† Octahedron edge.

tion of the angle and distance data, upon which some inferences concerned with hydrogen positions may be based, is reserved for later discussion.

Discussion

Inasmuch as the hydrogen positions have not been found experimentally, such premises as can be made concerning the chemical nature and bonding of the *w*-oxygen atoms in the structure must be based on the nature and geometrical arrangement of their nearest neighbors. The interatomic distances have normal values, but the configuration geometry is generally quite irregular. This is due in part to the character of the double chain, in which short Ga–O(*w*) bonds, and much longer O(*w*)–O(*w*) bonds are interconnected, and in which octahedrally directed bonds due to gallium restrict the possibility of regular geometrical arrangements about the *w*-oxygen atoms involved. Another possible cause of distortion is the high density of population in some regions of the crystal. For instance, oxygen *w*(1), as a consequence of its position as the shared corner of three gallium coordination octahedra, has eleven close oxygen or *w*-oxygen neighbors, all members of its own complex coordination array. (Table 3*a*). This is in sharp contrast with the more usual situation of *w*(2), an unshared corner, which has only four such neighbors. Obviously, there is no question of bond formation between atoms which are all bound to the same gallium atom. However, the directions in which such atoms may form other bonds is limited by the presence of the non-bonded neighbors.

The interconnected w-oxygen atoms

Fig. 3 illustrates most of the details to which reference is made in the discussion of the probable bonding scheme of the interconnected *w*-oxygen atoms, *w*(1), *w*(2) and *w*(3). Collected distance and angle data are given in Table 4.

The nearest neighbors of *w*(1) consist of three gallium atoms at an average distance of 2·13 Å, and one *w*(3) oxygen atom at 2·99 Å. The configuration is a very distorted tetrahedral array such that the six bond angles average 109·6 ± 10·3°. The nature of the surroundings leads to the conclusion that *w*(1) can be associated with only one hydrogen atom, located between *w*(1) and *w*(3). It is reasonable to assume that *w*(1) is a hydroxyl group, $(OH)^-$, strongly polarized by its gallium neighbors so that its charge distribution, approximately tetrahedral, has negative components directed toward the three gallium neighbors, and a single positive component extending in the direction of *w*(3). This interpretation of the behavior of the hydroxyl in the presence of strongly polarizing neighbors was first advanced by Bernal & Megaw (1935). The configuration is not uncommon. One example is the pyramidal ar-

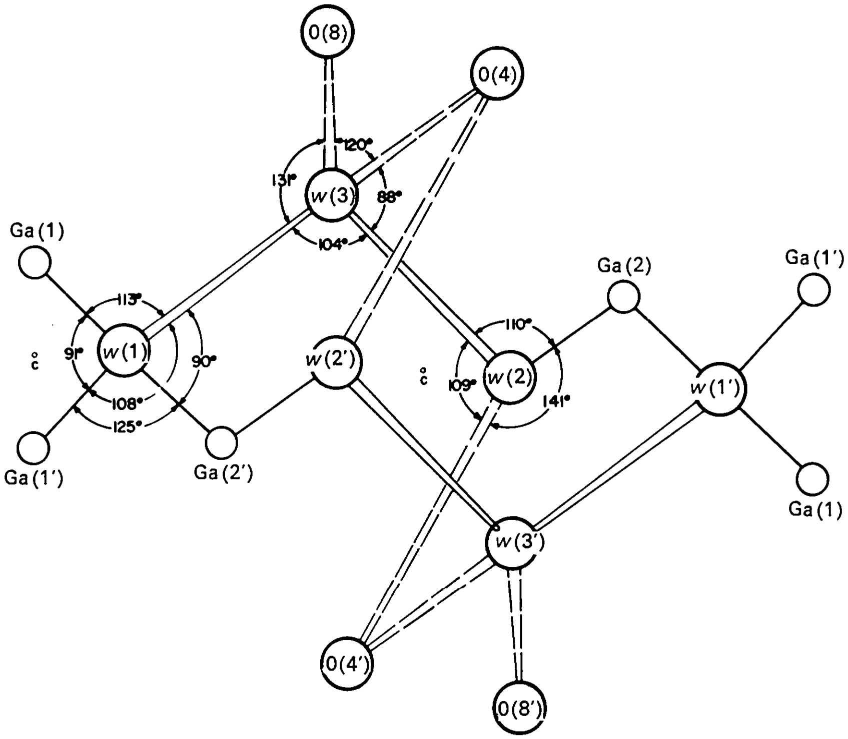

Fig. 3. Schematic diagram of the chain formed by gallium and water-oxygen atoms. The nearest phosphate oxygen neighbors, excepting those coordinated to gallium, are shown. Darts are used to indicate bonds in which hydrogens associated with *w*-oxygen atoms are presumably involved. The concentration of positive charge density is assumed to reside near the atom from which the blunt end of the dart originates.

rangement formed by three copper atoms about a hydroxyl in psuedomalachite, $Cu_5(OH)_4(PO_4)_2$ (Ghose, 1963).

The $w(2)$ and $w(3)$ oxygen atoms must first be considered together. As shown in Fig. 3, the succession of atoms, $w(1)$, $w(3)$ and $w(2)$ comprise a single chain segment attached to Ga(1), Ga(1′) and Ga(2′) at one end, and to Ga(2) at the other. It has already been predicted that a hydrogen atom, associated with $w(1)$, is located between $w(1)$ and $w(3)$. A second may be considered to lie between $w(2)$ and $w(3)$, the assignment being justified by the fact that the distance between the atoms, 2·66 Å, is acceptable, as are also the values of the angles, Ga–$w(2)$–$w(3)$ and $w(2)$–$w(3)$–$w(1)$, which are respectively 110° and 104°.

The chain segment is one of a pair, which are related by a center of symmetry. Centrosymmetrically related pairs of $w(3)$ atoms are more than 3·5 Å apart. Similarly related pairs of $w(2)$ atoms, also presumably nonbonded, are 3·12 Å apart. However, the distance between the $w(2)$ atom of one chain segment and the $w(3')$ of the companion chain is only 2·84 Å, suggestive of a possible direct cross-linking between the chains. This short distance is bridged by a phosphate oxygen atom, O(4), which is 2·81 Å from $w(2)$, and 2·91 Å from $w(3')$. There cannot be a hydrogen bond between $w(2)$ and $w(3')$, because such a bond would make an angle of only 70° with the hydroxyl bond direction $w(1')$ to (3), and also with the line directed from $w(2)$ to O(4). It may be that the interaction is of some other sort, or it may be that $w(2)$ and $w(3')$ are mutually unreactive in the direction across the chains, a condition that might be due to a particular distribution of charge density resulting from the formation of bonds in other directions. In any case, it will be assumed that the pair of chains are linked primarily by bonds to O(4).

If the possibility of some interaction with $w(3')$ is neglected, $w(2)$ has three neighbors within bonding distances; Ga(2), $w(3)$ and O(4). A hydrogen atom has previously been assigned to a location between $w(2)$ and $w(3)$; a second may be assumed to lie between $w(2)$ and O(4). The angle between these two bonds is 109°, and the whole configuration is essentially coplanar. Similar configurations are well known for water molecules attached to highly charged cations. Therefore, it is assumed that the two hydrogen atoms are primarily associated with the $w(2)$ oxygen atom, which may then be considered an H_2O species, strongly polarized toward gallium and forming hydrogen bonds of the unsymmetrical type to $w(3)$ and O(4), their lengths being, respectively, 2·66 and 2·81 Å.

For consistency with the hydrogen assignments so far made, $w(3)$ is required to have negatively charged regions both in the direction of the hydroxyl, $w(1)$, and in the direction of the water molecule, $w(2)$. Presumably, then, its positive charge components are interacting with neighboring phosphate oxygens. The five nearest phosphate oxygen atoms are O(8) at 2·77 Å; O(4) and O(3), (a tetrahedron edge), respectively at distances of 2·91 and 3·00 Å; and finally, O(6) and O(7) (another tetrahedron edge) respectively at distances of 3·12 and 3·18 Å. It is unlikely that all of these oxygen atoms are part of the $w(3)$ coordination. O(3) is unfavorably located; that is, it lies in a direction close to $w(2)$, toward which $w(3)$ has been assumed to be negatively polarized. O(6), in the opposite direction, is in a similar relation with respect to $w(1)$, and is also a bit distant, as is also O(7). If these are eliminated, then the contacts of $w(3)$ external to the chain are with the two nearest oxygen atoms O(8) and O(4). The configuration about $w(3)$, for want of a better description, may be compared to a grossly distorted tetrahedron, in which the pair of oxygen atoms are badly displaced from ideal positions with reference to $w(1)$ and $w(2)$. As its structural function, $w(3)$ connects successive gallium octahedra through $w(1)$ and $w(2)$ corners into a chain; and, in a direction roughly perpendicular to the chain direction, links a pair of neighboring chains through opposite octahedron corners, O(8) and O(4). It seems reasonable to consider $w(3)$ as a water molecule in a quasi-tetrahedral state, with negative charge concentrations toward $w(1)$ and $w(2)$, and positive components in the direction of O(4) and O(8).

The conclusions derived from a detailed examination of the double chain structure may be recapitulated as follows. There is little doubt that $w(1)$ is a hydroxyl group, and that four hydrogen atoms are involved in the binding system of $w(2)$ and $w(3)$. The latter have been described as H_2O species on the basis of reasonable assumptions. These assumptions involve, not only the general location of positive charges somewhere between pairs of atoms, but also their assignment to one or the other atom of the pair. The first is fairly straightfor-

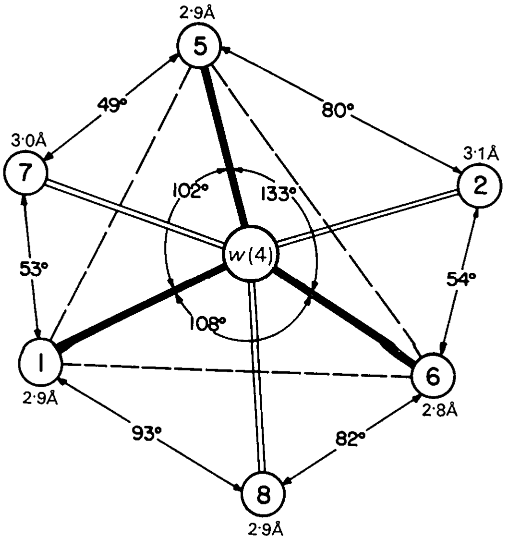

Fig. 4. Schematic diagram of the oxygen arrangement about $w(4)$. Each oxygen is tagged with its identifying number, and its distance from $w(4)$. The artificial device of sorting the oxygen atoms into two triangular arrangements is used merely as an aid for visualizing the geometry.

ward, but the second involves choices which, differently made, would lead to different conclusions concerning the species represented by $w(2)$ and $w(3)$. It follows that no unique chemical formula can be given without explicit information concerning the hydrogen positions. Therefore, on the basis of postulations which have been given in detail, a unit segment of the chain will be described as $[Ga_2(OH)(H_4O_2)]^{5+}$, where H_4O_2 probably represents a pair of interconnected H_2O species.

The isolated w-oxygen atom

Of the eight hydrogen atoms in the asymmetric unit, one has been assumed to be part of the charge density of the hydroxyl, $w(1)$, and four to be associated with $w(2)$ and $w(3)$. Inasmuch as there are no distances less than 3·4 Å between oxygen atoms of different phosphate groups except within gallium coordination octahedra, the three remaining hydrogen atoms are presumably associated with the last of the w-oxygen atoms to be discussed, $w(4)$.

Oxygen atom $w(4)$ lies in an oxygen-lined channel in the structure, 3·4 Å away from the nearest w-oxygen atom, and 4·00 Å away from the nearest gallium atom. It is surrounded, more or less cylindrically, by six phosphate oxygen atoms at distances ranging from 2·84 to 3·12 Å. Of these phosphate oxygen atoms, two pairs form octahedron edges, and one pair constitutes the edge of a phosphate tetrahedron. The distances between pairs so related are short – 2·73, 2·62, 2·44 Å – while other separations within the group of six range from 3·78 to 5·34 Å. Consequently, the group configuration cannot conveniently be referred to a regular geometrical figure. The arrangement is more easily described if, as in Fig. 4, the six oxygen atoms are pictured, in groups of three, as the corners of intersecting triangles. Then $w(4)$ is the apex of a low pyramid, completed by the three nearest phosphate oxygens, O(6), O(5) and O(1), at distances of 2·84, 2·88, and 2·89 Å respectively; while it is essentially coplanar with a triangular arrangement of the remaining three oxygen atoms at distances of 2·92, 2·99, and 3·12 Å.

Presumably, three hydrogen atoms are involved in the bonding system. On the basis of distances, at least four phosphate oxygen atoms must be included in the coordination group. It is possible that five, or perhaps all six may be part of it. In any case, it appears that one or more of the hydrogen atoms must be in a state of limited disorder.

It is interesting, at this point, to review briefly some established structural results concerned with the association of three hydrogen atoms with an oxygen. The classical example is the hydronium group, $(H_3O)^+$, the structural characteristics of which have been studied mainly in the crystals of hydrated acids. In general, hydronium forms three directed hydrogen bonds, and has the configuration of a flat trigonal pyramid with oxygen at the apex. This is the situation in $(H_3O)NO_3$, nitric acid monohydrate, (Luzzati, 1951); in $(H_3O)NO_3 . 2H_2O$, nitric acid trihydrate (Luzzati, 1953); and in $(H_3O)Cl$, hydrochloric acid monohydrate (Yoon & Carpenter, 1959). However, in $(H_3O)ClO_4$, perchloric acid monohydrate (Lee & Carpenter, 1959) the group, apparently disordered, is surrounded by twelve perchlorate oxygen atoms at distances of 2·9 to 3·4 Å. A neutron diffraction study of the crystal (Smith & Levy, 1959) indicates that, though disordered, the group is not freely rotating, and that some hydrogen bonding occurs.

The three hydrogen atoms in the neighborhood of $w(4)$ must be supposed to function as links between $w(4)$ and various surrounding phosphate oxygen atoms. The manner of their distribution between positions closer to $w(4)$, or closer to a phosphate oxygen atom to form, perhaps, $(HPO_4)^{2-}$, must be known in order to classify $w(4)$ as a definite chemical species. Inasmuch as the geometrical data give little basis for speculation concerning specific hydrogen positions, it seems best to describe the $w(4)$ oxygen system in terms of its components, that is, as a water molecule associated in some manner with an additional hydrogen atom. For this we write $[H_2O . H]^-$, for the purposes of description, and without implication of the role of any of the hydrogen atoms.

Conclusion

The results of this investigation may be briefly summarized as follows. A previously unknown hydrated form of gallium phosphate has been prepared. Though the hydrogen positions have not been determined experimentally, the atomic arrangement suggests that the compound is a hydrated basic salt. On the basis of assumed hydrogen positions, a structural formulation may be written as $[Ga_2(OH)(H_2O)_2]\ (H_2O)(H)(PO_4)_2$. In this crystal, gallium does not function as a single ion but as part of an infinite hydrated hydroxy chain complex, the asymmetric unit of which is given within the square brackets. The hydrogen atoms in the grouping $(H_2O . H)^+$ are apparently disordered.

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Structure Cristalline du Fluorotitanate Acide de Sodium, Na_3HTiF_8

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The crystal structure of sodium fluorotitanate–sodium bifluoride has been determined with three-dimensional data with the use of Cu $K\alpha$ radiation. Na_3HTiF_8 is orthorhombic, *Cmcm*, with $a=7{\cdot}182$, $b=13{\cdot}86$, $c=6{\cdot}538$ Å and four molecules per unit cell. Fourier and least-squares methods were used to determine positional coordinates. The structure is an aggregate of K^+, octahedral $[TiF_6]^{2-}$ and $[HF_2]^-$ ions; the double salt formula $Na_2TiF_6 . NaHF_2$ is therefore appropriate.

Introduction

Il semble que Marignac (1859) soit le premier à avoir signalé l'existence du fluorotitanate acide de sodium Na_3HTiF_8, du fluorostannate acide de potassium K_3HSnF_8 et de l'oxofluoroniobate acide de potassium K_3HNbOF_7. C'est à Brauner (1894) que nous devons la préparation du fluoroplombate acide de potassium K_3HPbF_8.

Hoard & Martin (1941) ont montré que le composé monoclinique K_3HNbOF_7 est un sel double contenant des ions octaédriques $[NbOF_5]^-$, des ions linéaires $[HF_2]^-$ et des ions K^+. Weiss, Chevrier & Fischer (1965) ont montré que le composé K_3HSnF_8 présente une structure très voisine de celle de K_3HNbOF_7. Dove (1959), par l'étude du spectre d'absorption infrarouge du composé orthorhombique Na_3HTiF_8, avait conclu à l'existence de deux types d'ions $[HF_2]^-$ dans la maille. Afin de vérifier les hypothèses de Dove, nous avons déterminé la structure de Na_3HTiF_8.

Données expérimentales

Le fluorotitanate acide de sodium a été préparé selon une méthode de Marignac. Les cristaux appartiennent au système orthorhombique, les formes dominantes sont généralement: {110}, {001}, {010} et {120}. Les valeurs des paramètres cristallins trouvées sont:

$$a=\ 7{,}182\pm0{,}008\ \text{Å}$$
$$b=13{,}86\ \ \pm0{,}01$$
$$c=\ 6{,}538\pm0{,}006$$
$$\lambda\ \text{Cu}\ K\alpha=1{,}5418\ \text{Å}\ .$$

La densité mesurée par picnométrie est de 2,80. La densité calculée pour quatre motifs Na_3HTiF_8 par maille est de 2,76.

Les réflexions *hkl* telles que $h+k=2n+1$ et *h0l* telles que $l=2n+1$ sont systématiquement éteintes. Les groupes de symétrie possibles sont *Cmcm* et *Cmc*2.

Les intensités diffractées ont été enregistrées à l'aide d'un rétigraphe muni d'un dispositif intégrateur. Le cristal utilisé avait la forme d'un cylindre d'axe [001] et de 0,2 mm de diamètre. Les strates *hk*0 à *hk*5 ont été enregistrées ($\sin\theta_{\max}=0{,}97$; 248 réflexions indépendantes). Ces intensités ont été mesurées par microdensitométrie et corrigées des facteurs de Lorentz, polarisation et absorption. Les facteurs d'absorption ont été calculés à l'aide des tables de Bond (1959).

Détermination de la structure

La projection de la fonction de Patterson suivant l'axe [001] a été interprétée par la méthode de la convergence des vecteurs, appliquée au pseudo-atome Ti–Ti. Tous les atomes, sauf les atomes de fluor F(3) et F(4) sont