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The Crystal Structure of Magnesium Phosphite Hexahydrate, $MgHPO_3.6H_2O$

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The crystal structure of magnesium phosphite hexahydrate, $MgHPO_3.6H_2O$, has been determined by Fourier methods. The lattice is rhombohedral, with unit-cell dimensions $a_R = 5{\cdot}96$ Å, $\alpha = 96° 24'$. The space group is $R3$ and the Mg, P and H atoms lie on the unique axis. The structure is built from discrete tetrahedral $[HPO_3]^{2-}$ ions and octahedral $Mg^{2+}(H_2O)_6$ groups, which are linked together in three dimensions by a continuous system of hydrogen bonds. The crystals are isomorphous with those of magnesium sulphite hexahydrate, $MgSO_3.6H_2O$, which probably contain an isostructural arrangement.

Introduction

Phosphorous acid, H_3PO_3, is dibasic, and its crystalline salts are usually assumed to contain discrete tetrahedral $[HPO_3]^{2-}$ ions in which the hydrogen atom is linked directly to phosphorus. Evidence for this configuration is provided by infra-red spectra (Corbridge & Lowe, 1954) and Raman spectra (Simon & Fehér, 1937), but no detailed X-ray studies of crystalline phosphites have been reported. The existence of approximately tetrahedral $[H_2PO_2]^-$ ions in hypophosphites has been demonstrated in the crystal structures of ammonium hypophosphite $(NH_4)H_2PO_2$ (Zachariasen & Mooney, 1934) and magnesium hypophosphite $Mg(H_2PO_2)_2$ (Pedrazuela, Garcia-Blanco & Rivoir, 1953).

Unit cell and space group

Small, hemimorphic, trigonal pyramidal crystals were obtained by evaporation of an aqueous solution of the salt. The dimensions of the hexagonal unit cell, determined from rotation photographs, were

$$[a] = 8{\cdot}88,\ [c] = 9{\cdot}10\ \text{Å}\ .$$

The corresponding rhombohedral constants are

$$[a_R] = 5{\cdot}96\ \text{Å},\ \alpha = 96°\ 24'\ .$$

The density, determined by flotation, was 1·708 g.cm.$^{-3}$, while that calculated for the hexagonal cell, assuming 3 units of $MgHPO_3.6H_2O$, was 1·703 g.cm.$^{-3}$.

The symmetry of [*c*]-axis Weissenberg and oscillation photographs indicated a rhombohedral lattice. Indexing of zero and 1st layer [*c*]- and [*a*]-axis Weissenberg photographs revealed that reflexions were absent for $-h+k+l = 3n$, and the intensities of spots on the [*c*]-axis zero-layer-line photograph were such that $I_{hki0} \neq I_{khi0}$. The crystals were found to be strongly pyroelectric and space group $R3$ was adopted.

Intensity data

Experimental intensity data were obtained from zero-layer-line [*c*]- and [*a*]-axis Weissenberg photographs taken with Cu $K\alpha$ radiation. A multiple-film technique employing six films for each layer line was used. The intensities were estimated visually, and Lorentz and polarization corrections were made in the usual way. Absorption effects were minimized by using small equant crystals $\sim 0{\cdot}3$ mm. The structure amplitudes were put on an absolute scale by comparison with the calculated values during later stages of the analysis. A total of 180 different spots were estimated, giving a final list of 74 non-equivalent $\{hki0\}$- and $\{0kil\}$-type reflexions.

Structure determination

In space group $R3$ the special and general positions in the hexagonal cell are:

$$
\begin{aligned}
n = 3(a)\ & 0, 0, z;\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{2}{3}+z;\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{3}+z.\\
n = 9(b)\ & x, y, z;\ \bar{y}, x-y, z;\ y-x, \bar{x}, z;\\
& \tfrac{1}{3}+x, \tfrac{2}{3}+y, \tfrac{2}{3}+z;\ \tfrac{1}{3}-y, \tfrac{2}{3}+(x-y), \tfrac{2}{3}+z;\\
& \tfrac{1}{3}+(y-x), \tfrac{2}{3}-x, \tfrac{2}{3}+z;\ \tfrac{2}{3}+x, \tfrac{1}{3}+y, \tfrac{1}{3}+z;\\
& \tfrac{2}{3}-y, \tfrac{1}{3}+(x-y), \tfrac{1}{3}+z;\ \tfrac{2}{3}+(y-x), \tfrac{1}{3}-x, \tfrac{1}{3}+z.
\end{aligned}
$$

Since the hexagonal cell contains three each of Mg, P and H atoms, they must occupy three sets of positions (*a*). Such an arrangement would be consistent with a tetrahedral HPO_3 ion lying with the P–H linkage coincident with the threefold axis and with the remaining oxygens disposed with trigonal symmetry in positions (*b*). At this stage it was also assumed that the 18 water molecules in the cell would occupy two sets of positions (*b*), which would enable them to be grouped octahedrally round the magnesium atoms.

A Patterson synthesis for the [*c*]-axis projection is shown in Fig. 1. Structure-factor calculations were carried out commencing with the water molecules in positions *A* and *B* and the oxygen atom in one of these. The coordinates were refined by trial-and-error work in conjunction with Fourier syntheses and the final electron density map is shown in Fig. 2(*a*). At this stage the agreement factor $R = \Sigma|F_o|-|F_c|\div\Sigma|F_o|$ was 13·5% and could not be reduced further.

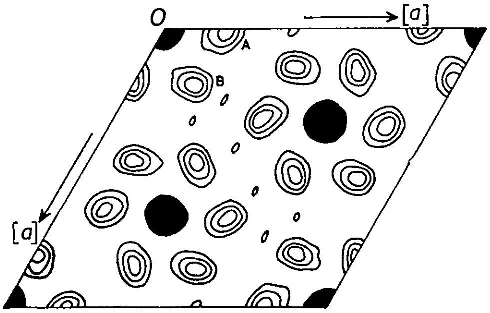


Fig. 1. Patterson synthesis, [c] projection.

Refinement of the (x, y) parameters was then effected by two difference syntheses using the (F_o-F_c) values, and the final agreement factor for this projection was $R = 7{\cdot}6\%$.

Interatomic distances of P–O ~ 1·51 Å, and Mg–W ~ 2·05 Å were assumed and an approximate set of *z* parameters was derived from packing considerations. The Mg^{2+} ion was placed at $z = 0$ and trial-and-error work was carried out in conjunction with Fourier syntheses. The final synthesis for the [*a*] projection is shown in Fig. 2(*b*). Further refinement of the *z* parameters was obtained from two difference syntheses with the $\{0kil\}$ terms, and the agreement factor reduced from $R = 22{\cdot}5\%$ to $R = 16{\cdot}3\%$. A significant indication of the hydrogen position was not obtained.

The final atomic coordinates from the two projections are listed in Table 1. The fact that R_{hki0} reduced to about half the value of R_{0kil} is possibly connected with the presence of both the phosphorus and magnesium atoms at the origin in the former projection. The calculated bond lengths are probably accurate to within about ±0·05 Å, taking into consideration the shifts produced by the difference syntheses and the sensitivity of R_{hki0} and R_{0kil} to further coordinate changes. Scattering factors for Mg^{2+}, O^- and P were obtained from the *International Tables* and a temperature factor of $B = 0{\cdot}5$ Å^2 was found to give the best structure-factor agreement.

Table 1. *Atomic coordinates*

	x	*y*	*z*
Mg	0	0	0
P	0	0	0·488
H	0	0	~ 0·65
O	0·130	0·180	0·435
W_1	0·010	0·205	0·882
W_2	0·183	0·198	0·140

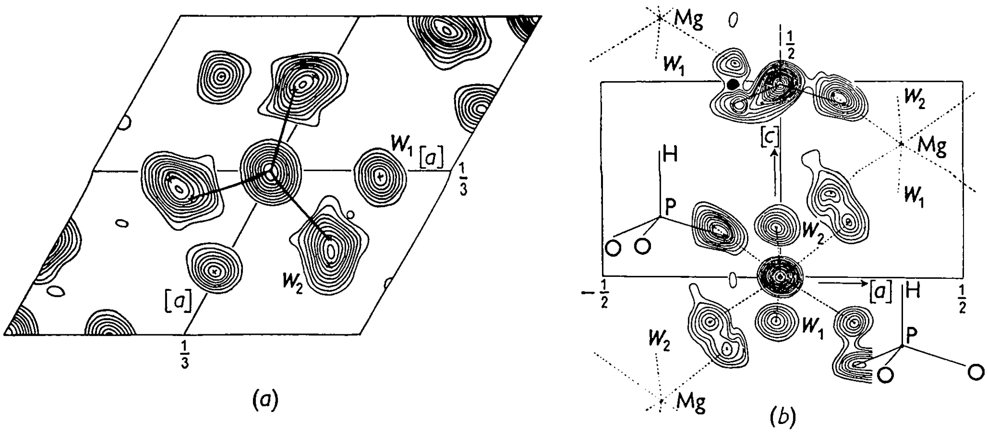


Fig. 2. (*a*) Electron density, [*c*]-axis projection. (*b*) Electron density, [*a*]-axis projection. Contours at arbitrary intervals, with lowest level approximately 1·5 e.Å^{-2}.

Table 2. *Observed and calculated structure amplitudes*

$hk\bar{i}0$	F_o	F_c	α (°)	$0k\bar{i}l$	F_o	F_c	α (°)	$0k\bar{i}l$	F_o	F_c	α (°)
3030	37	44	73·5	0221	26	19	102·2	0111	22	19	266·4
6060	77	77	359·5	0551	43	36	16·8	0441	33	35	61·9
9090	36	31	31·2	0112	79	91	337·6	0771	11	16	240·1
1120	62	73	353·7	0442	33	31	330·0	0222	71	71	347·7
4150	79	86	358·6	0772	37	37	6·1	0552	45	47	354·4
7180	25	24	35·7	0003	99	115	159·7	0882	24	24	351·4
2240	32	29	266·4	0333	44	37	14·7	0333	16	33	97·8
5270	59	57	354·2	0663	35	32	163·5	0663	26	26	174·7
8,2,10,0	12	13	2·6	0224	51	50	1·7	0993	14	19	134·4
3360	31	29	341·6	0554	28	25	235·0	0114	41	37	82·4
6390	28	29	336·0	0884	31	31	29·7	0444	40	36	320·2
1450	63	65	345·8	0115	35	23	119·6	0774	30	32	9·3
4480	29	29	13·0	0445	8	10	214·6	0225	22	5	80·6
7,4,11,0	21	17	342·1	0775	12	13	114·8	0555	28	31	155·2
2570	33	32	58·2	0006	45	37	310·0	0885	6	12	74·2
5,5,10,0	51	48	348·1	0336	31	32	12·2	0336	48	53	352·2
3690	26	26	45·5	0666	34	33	335·3	0666	28	25	349·9
1780	14	9	31·0	0227	11	5	225·0	0117	47	38	351·0
4,7,11,0	27	28	333·4	0557	34	34	39·2	0447	29	13	276·5
2,8,10,0	25	23	0·8	0118	37	35	7·3	0777	6	8	132·1
				0448	38	48	8·0	0228	31	20	348·5
				0778	20	26	314·5	0558	45	51	336·9
				0009	34	35	21·1	0339	23	9	183·7
				0339	15	12	181·4	0669	13	8	31·8
				0669	19	18	56·0	0,1,1,10	12	22	313·4
				0,2,2,10	27	28	350·2	0,4,4,10	19	17	13·1
				0,5,5,10	14	22	331·0	0,2,2,11	16	11	42·9

Discussion of structure

The phosphite ion is tetrahedral and has threefold symmetry about the P–H bond direction, which is coincident with a threefold symmetry axis in the unit cell. Diagrams of the structure are shown in Figs. 3 and 4.

The experimental P–O distance of 1·51 Å lies close to values found in related oxy ions, e.g. 1·51 Å in $NaHPO_3NH_2$ (Hobbs, Corbridge & Raistrick, 1953), 1·51 Å in $NH_4H_2PO_2$ (Zachariasen & Mooney, 1934), 1·52 Å in $Mg(H_2PO_2)_2$ (Pedrazuela *et al.*, 1953), 1·54 Å in KH_2PO_4 (Bacon & Pease, 1953), 1·54 Å (average) in $CaHPO_4$ (MacLennan & Beevers, 1955), 1·52 Å (average) in $Ca(H_2PO_4)_2H_2O$. (MacLennan & Beevers, 1956).

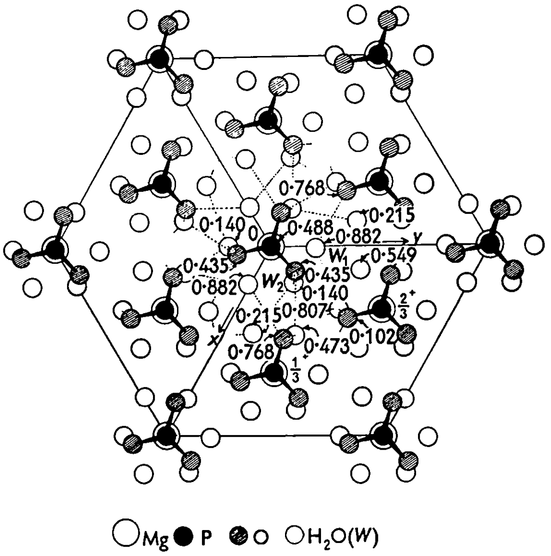


Fig. 3. Magnesium phosphite hexahydrate structure, [*c*]-axis projection. Numerals represent *z* coordinates.

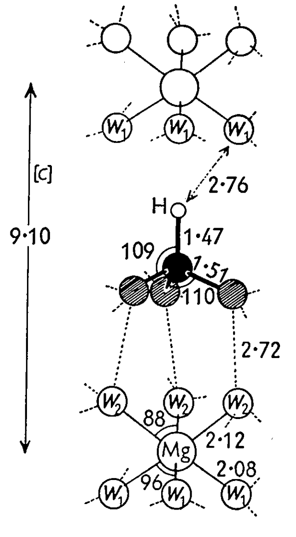
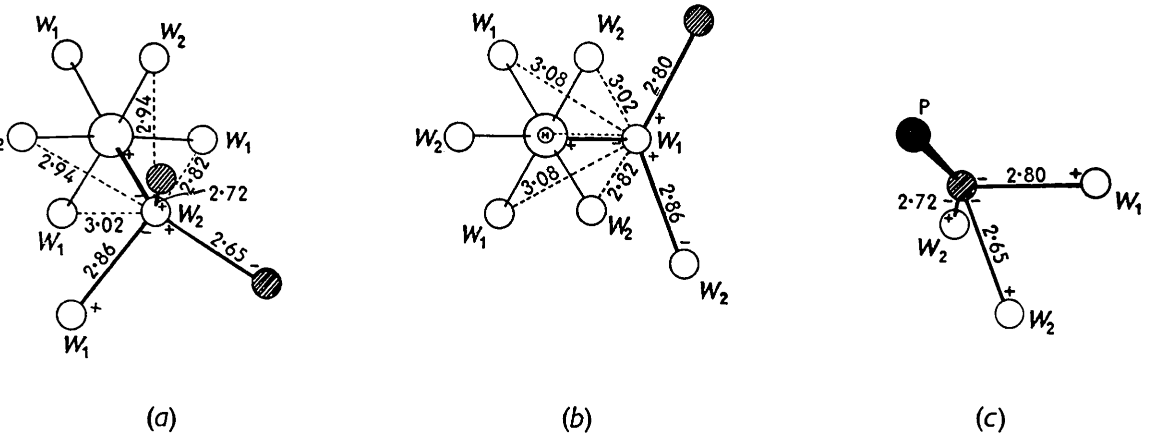


Fig. 4. Atomic arrangement round the threefold axis, viewed parallel to [*a*]. All distances in Ångström units and angles in degrees.

The Mg^{2+} cations are coordinated octahedrally by the six water molecules at a mean distance of 2·10 Å. This may be compared with the sum of Pauling ionic radii (2·05 Å) and the octahedral values 2·01 and 2·07 Å found in $Mg(H_2PO_2)_2$ (Pedrazuela *et al.*, 1953) and 2·04 Å in $Mg(C_6H_5SO_3)_26H_2O$ (Broomhead & Nicol, 1948).



(a) (b) (c)

Fig. 5. Probable hydrogen bonding scheme. Broken lines represent contacts between water molecules in the same octahedral grouping and full lines correspond to broken lines in Figs. 3 and 4. All distances in Ångström units.

Several close water–oxygen and water–water contacts are made in the structure and the environments of these molecules are shown in Fig. 5. If the close water–water contacts in the same octahedral grouping are ignored, the hydrogen bond system is probably as indicated. The observed distances range from 2·65 to 2·86 Å and probably represent 'long' hydrogen bonds, which link the $[HPO_3]^{2-}$ and $[Mg(H_2O)_6]^{2+}$ groups in a continuous three-dimensional network.

The close coordination (i.e. at less than about 3·3 Å) of water molecules by more groups than are apparently required by the tetrahedral charge rule occurs, for example, in $BaS_4O_6.2H_2O$ (Foss, Furberg & Zachariasen, 1954), and $LiClO_4.3H_2O$ (West, 1934), and may be found in other hydrate structures, particularly those with octahedral coordination groups.

W_2 is coordinated tetrahedrally by Mg, W_1 and two oxygen atoms (Fig. 5(*a*)), while the configuration of Mg, W_2 and O round W_1 is nearer that of a planar trigonal arrangement (Fig. 5(*b*)). Assuming P–H$\sim$1·47 Å, the calculated H–W_1 distance is 2·76 Å, and this hydrogen cannot therefore be considered as taking part in hydrogen bond formation. Each oxygen atom makes three contacts disposed approximately tetrahedrally to neighbouring water molecules (Fig. 5(*c*)).

Isomorphism

During the investigation it was noticed that magnesium phosphite hexahydrate crystals were isomorphous with those of magnesium sulphite hexahydrate. Earlier work (Klasens, Perdok & Terpstra, 1936) has shown this latter salt to be rhombohedral with $[a] = 8{\cdot}82$ Å, $[c] = 9{\cdot}05$ Å, space group *R*3, and with a unit cell content of three molecules of $MgSO_3.6H_2O$.

Although the structure of this salt was not worked out, a general packing scheme similar to that found in magnesium phosphite was postulated. The trigonal pyramidal configuration of the sulphite ion has been demonstrated in the crystal structure of Na_2SO_3 (Zachariasen & Buckley, 1931).

Powder photographs were taken to confirm the isomorphism, and a very similar distribution of intensities in the two salts was revealed. The hexahydrates of magnesium phosphite and magnesium sulphite presumably contain isostructural arrangements with the sulphite and phosphite ions lying in corresponding positions round the trigonal axes.

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