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A REFINEMENT OF THE CRYSTAL STRUCTURE OF $CaHPO_4$ (SYNTHETIC MONETITE)

by

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Abstract

$CaHPO_4$, synthetic monetite, crystallizes in the triclinic unit cell $\underline{a}$ = 6.910(1) Å, $\underline{b}$ = 6.627(2) Å, $\underline{c}$ = 6.998(2) Å, α = 96.34(2)°, β = 103.82(2)°, γ = 88.33(2)° at 25°C with cell contents of 4[$CaHPO_4$]. The structure has been refined in space-group $P\bar{1}$ by the method of least squares to $\underline{R}_w$ = 0.032, $\underline{R}$ = 0.031 using 3738 observed reflections measured on a diffractometer. Corrections were made for anomalous dispersion, absorption and isotropic secondary extinction.

The structure may be considered to consist of $CaHPO_4$ chains bonded together by Ca...O bonds and three types of hydrogen bonds. One type of hydrogen bond, O(1)-H(1)...O(5), is normal but is at the short end of the normal range with O(1)...O(5) = 2.565(1) Å; one, O(7)-H(2)...O(7'), is very short with O(7)...O(7') = 2.458(2) Å and is across a nominal center of symmetry; and one, O(6)-H(3)...O(8) where O(6)...O(8) = 2.669(1) Å, is in the normal range but is presumed to be statistically disordered, with hydrogen covalently bonded to half of the O(6) atoms on average. The P-O distances support the choice of these hydrogen positions. The calculated position of H(3) suggests that it is coordinated to the O(6,8) edge of the adjacent $P(2)O_4$ group. The two possible sites for H(3) are then 1.45 Å apart and simultaneous occupation of these two sites is improbable. The strong

hydrogen bonding may distort $CaHPO_4$ from the orthorhombic $CaSO_4$ structure to triclinic. Ca(1) is coordinated to seven oxygens in an approximate pentagonal bipyramid with Ca(1)...O distances ranging from 2.2951(9) Å to 2.763(1) Å. Ca(2) is coordinated to eight oxygens with Ca(2)...O distances ranging from 2.379(1) Å to 2.5718(9) Å, which all indicate strong Ca...O bonding. The Ca coordinations in several calcium phosphates and related compounds are compared.

Introduction

The general features of the crystal structure of $CaHPO_4$ were determined by MacLennan and Beevers (1955), who refined the structure to $\underline{R}$ = 0.20 using hk0, h0ℓ and 0kℓ photographic data. They gave no positions for the hydrogen atoms because they considered the structural details to be obscured by the large standard deviations (> 0.05 Å) associated with the interatomic distances.

The structure was refined to $\underline{R}$ = 0.15 by Jones and Cruickshank (1961) using 790 reflections collected and measured by MacLennan and Beevers but uncorrected for high absorption. Possible positions for the hydrogen atoms given by Jones and Cruickshank were based on the P-O and O...O distances they obtained. Curry, Denne and Jones (1968) measured 381 reflections from a large single crystal of $CaHPO_4$ at room temperature using neutron diffraction and refined the occupational parameters of possible hydrogen sites while keeping the parameters of the heavier atoms fixed at the fairly imprecise and ambiguous values obtained in the X-ray refinements reported earlier by Jones and Cruickshank. On the basis of these results, hydrogens were assigned to the O(1) atoms and to half of the O(6) and O(7) atoms in the structure. This work has been continued by Denne and Jones (1969).

The heat capacity versus temperature curve of $CaHPO_4$ has been observed (Egan and Wakefield, 1964) to contain an abnormality (a broad hump beginning at 223°K with a maximum at 273°K).

Although neither the line width nor the second moment changed significantly in NMR results obtained by Jones and Cruickshank on a sample of $CaHPO_4$ cooled from room temperature to liquid-nitrogen temperature, hydrogen-motion remains a plausible explanation for the anomaly in the heat capacity curve for $CaHPO_4$. It is not yet known whether the anomaly arises from rapid hydrogen motion or from an order-disorder process. As a precursor to work at two or more temperatures on the crystal structure of $CaHPO_4$ using neutron diffraction and to intended spectral investigations, we have refined the crystal structure using new X-ray data collected from a single crystal. The precision of the structural features has been greatly improved and these features are now more consistent with the chemical aspects of the structure. The hydrogen atoms have been located approximately. The bonding scheme given by Jones and Cruickshank and Curry, Denne and Jones is confirmed.

Data collection and structure refinement

The crystal used in the collection of X-ray data was colorless and approximately rhombic in shape with an edge of about 0.15 mm and a volume of 0.004 mm^3. It was taken from a sample of $CaHPO_4$ grown by cyclic dilution and concentration of the supernatant aqueous solution over a mixture of $CaHPO_4$ and $Ca_5(PO_4)_3OH$ in the lower chamber of a Soxhlet apparatus. It was attached to the goniometer head in our usual way (Dickens and Bowen, 1971a).

formula (ideal): $CaHPO_4$
cell: triclinic
$\underline{a}$ = 6.910(1) Å at 25°C
$\underline{b}$ = 6.627(2)
$\underline{c}$ = 6.998(2)
α = 96.34(2)°
β = 103.82(2)
γ = 88.33(2)
volume = 390.27 $Å^3$
space-group $P\bar{1}$ assumed; cell contents 4[$CaHPO_4$]
calculated density 2.933 $g \cdot cm^{-3}$; observed density 2.929 $g \cdot cm^{-3}$ (de Schulten, 1901).

The X-ray data were measured using the general procedure given in Dickens and Bowen (1971b). θ-2θ scans were done at 1°/min for 2θ, and the backgrounds were counted for 10 sec each. 8849 reflections were collected from two hemispheres of the reciprocal lattice; $hk\ell$ and $\bar{h}\bar{k}\ell$ pairs were merged into a unique set of 3861 reflections, of which 3738 were "observed" and 123 were "unobserved". After correction for absorption, symmetrically equivalent $F_{hk\ell}$'s agreed within 2% on average. Unobserved reflections were those less than 2σ(I) above background. The intensities were corrected for absorption as described in Dickens and Bowen (1971a and 1971b). μ(Mo) was taken to be 21.3 cm^{-1}. The maximum and minimum transmission factors were 0.796 and 0.701, respectively. 2θ for the highly oriented graphite monochromator crystal was 12.32°.

The structure as given by Jones and Cruickshank was refined isotropically using the program RFINE (written by L. W. Finger of the Carnegie Institute of Washington) to $\underline{R}_w$ = 0.086, $\underline{R}$ = 0.089 in two cycles (average shift/error for second cycle = 0.91) and then to $\underline{R}_w$ = 0.035, $\underline{R}$ = 0.032 in two cycles of anisotropic refinement. The scattering factors were those of the neutral atoms and were taken from Cromer and Mann (1968).

The hydrogen atoms were found in a difference electron-density synthesis as peaks of 0.75, 0.77 and 0.34 electrons·$Å^{-3}$ for the hydrogens H(1), H(2) and H(3) on O(1), O(7) and O(6), respectively. H(3) is a hydrogen atom disordered over two widely separated sites, while H(2) is either in a centered hydrogen bond or in two sites which are very close to each other. The background in the map was 0.50 electrons·$Å^{-3}$; steric considerations were used to find the "half" hydrogen atom H(3) on O(6). The structure was refined for (i) two more cycles with these hydrogens included with fixed isotropic thermal parameters of 1 $Å^2$, and with H(2) fixed at the origin, (ii) two cycles in which the isotropic extinction parameter, r in the notation of Zachariasen (1967), was also varied, and (iii) three cycles in which allowance was also made for the anomalous scattering of Ca and P. The values for f′ and f″ were taken from Cromer (1965).

In these last three cycles, R_w decreased from 0.035 to 0.032, R changed from 0.032 to 0.031, and the extinction parameter changed from 0.0021(6) cm to 0.000009(6) cm. It appears that there is a high correlation between the corrections for secondary extinction and anomalous dispersion. The largest correlation coefficient was 0.46 between the extinction and scale parameters. The next largest was 0.40 between x and z of O(8). The position of H(3) was not well defined in any of the refinements. It wandered from 1.24 Å to 1.58 Å from O(6), with O(6)-H...O(8) angles of about 150-160°. From the P-O bond lengths observed here (see later) and from the findings of Curry, Denne and Jones, H(3) is believed to be covalently bonded to O(6).

The structural parameters obtained in the refinements which included corrections for extinction and anomalous dispersion are given in table 1. In general, the precision is improved by a factor of 15 to 20 over the previous determinations. The structural details in the PO_4 groups are more consistent with the observed chemistry and hence are also considered to be more accurate than earlier values. The observed and calculated structure factors are given in table 2. Three sets of hydrogen positions from (i) the Fourier difference synthesis, (ii) the least-squares refinements and (iii) calculations to idealize the HPO_4^{2-} geometry (see later) are given in table 3. The calculated hydrogen positions were used in the calculation of interatomic distances mentioned in table 4.

Description of the structure

The structure of $CaHPO_4$ (Fig. 1) contains, parallel to [010], distorted versions of the $Ca\text{-}XO_4$ chains found in several other calcium phosphates and related compounds, e.g., $Ca(H_2PO_4)_2 \cdot H_2O$ (Dickens and Bowen, 1971b; Jones and Cruickshank, 1961; MacLennan and Beevers, 1956); $CaHPO_4 \cdot 2H_2O$ (Curry and Jones, 1970; Jones and Smith, 1962; Beevers, 1958); $CaSO_4 \cdot 2H_2O$ (Atoji and Rundle, 1958) and $CaSO_4$ (Hohne, 1962; Cheng and Zussmann, 1963). In $CaHPO_4$, one set of chains consists of the Ca(1) and $P(2)O_4$ ions,

and the other set consists of the Ca(2) and $P(1)O_4$ ions. The usual chain linkage of two XO_4 edges to each Ca ion has been reduced to one PO_4 edge and a PO_4 apex in $CaHPO_4$.

The Ca ion environment

The details of the environments of the two crystallographically different Ca ions in the structure are given in Table 4 and Figs. 2a and 2b. Ca(1) is coordinated (Fig. 2a) to seven oxygens, six [O(4,8,1,2,2′,6)] with Ca...O distances in the range 2.295 Å to 2.450 Å, which denote strong Ca...O bonding, and one [O(7)] at 2.763 Å, which is at the upper end of the normal range. The O(6,7) PO_4 edge and the PO_4 apexes O(2), O(8) and O(4) are arranged in an approximately planar pentagon; O(1) and O(2′) are the apexes of an approximately pentagonal bipyramid. This type of coordination is common in calcium phosphates. As is the case in other compounds where Ca-XO_4 chains are found, the $P(2)O_4$ edge [O(6,7)] coordination to Ca(1) in the Ca(1)-$P(2)O_4$ chain involves the longest Ca...O distances, which is in accord with Pauling's rule (Pauling, 1960) concerning repulsion between (in this case) Ca and P. Only the apex O(8) of the opposite $P(2)O_4$ edge O(5,8) is coordinated to Ca(1) and is involved in the second shortest Ca...O bond. The Ca(1)...P(2) distances along the direction of the Ca(1)-$P(2)O_4$ chain are 3.2380(4) Å for edge coordination of the $P(2)O_4$ group to Ca(1) and 3.4496(4) Å for apex coordination, which shows that, as judged from the Ca...P distances in this and other calcium phosphates, the Ca(1)...P(2) repulsion is normal in both cases.

Ca(2) is coordinated (Fig. 2b) to eight oxygens [O(3,5,4,3′, 8,7,6,2)] with Ca...O distances in the range 2.379 Å to 2.572 Å. All these bonds are strong. In the Ca(2) coordination geometry, O(8), O(6), O(5), O(7), and O(3′) lie in an approximate pentagon. O(3) lies at one apex of an approximate pentagonal bipyramid, and the center of the O(2,4) edge of the $P(1)O_4$ group lies at the remaining apex position. The chain involving Ca(2) includes the $P(1)O_4$ group coordinated in a manner very similar to the coordination of the $P(2)O_4$ group to Ca(1). Both chain directions are vertical in Figures 2a and 2b. The Ca(2)...P(1) distances for the O(2,4) edge and the O(3) apex coordination in the Ca(2)-$P(1)O_4$ chain are 3.1005(4) Å and 3.5750(4) Å, respectively. (Figures 2c to 2e are mentioned in the Discussion, where the calcium coordinations in $CaHPO_4$ and several related compounds are compared.)

The PO_4 groups and their environments

The details of the two unique PO_4 groups and their environments are given in Table 4 and Figures 3a and 3b. In the $P(1)O_4$ group (Fig. 3a), the O(2,4) edge is the only edge coordinated to Ca. The O(2)-P(1)-O(4) angle is less than the tetrahedral angle, in accord with Pauling's rule. The two other O-P-O angles in the $P(1)O_4$ group which are less also than the tetrahedral angle involve oxygens O(1) which is covalently bonded to hydrogen. Such P-O bonds may be expected to contain less double bond character than P-O bonds where the oxygen is "terminal" and O-P-O angles with one or both oxygens of this type are expected to be less than tetrahedral (Cruickshank, 1961). Similar angles have been observed in the recent refinements of $Ca(H_2PO_4)_2 \cdot H_2O$ (Dickens and Bowen, 1971b) and $CaPO_3F \cdot 2H_2O$ (Perloff, 1971). The O(1)-P(1)-O(3) angle in $CaHPO_4$ is, however, not less than this tetrahedral angle, although O(1) is involved in the angle.

The P(1)-O distances (table 5) overwhelmingly point to O(1) as being covalently bonded to hydrogen. (P(1)-O(2) is the second longest, 1.5397 Å, of the P(1)-O bonds; this apparent lengthening compared to P(1)-O(3) and P(1)-O(4) is probably due to the influence of the three Ca ions bonded to O(2).) O(1) is the donor in the hydrogen bond of H(1) to O(5); the O(1)...O(5) distance, 2.565 Å, is very short, and the H(1)...O(5) distance, 1.59 Å, indicates that there is a strong hydrogen bond between these two atoms. (Distances and angles involving hydrogen atoms were obtained using the calculated hydrogen positions.)

In the $P(2)O_4$ group (Fig. 3b), P(2)-O(6) and P(2)-O(7) are the longest P-O distances and are about equal with an average value of 1.547 Å. This value is close to being halfway (1.554 Å) between (i) the average (1.516 Å) of the P(1)-O(3) and P(1)-O(4) distances, which are the P(1)-O distances least disturbed by cationic and hydrogen bonding, and (ii) the P(1)-O(1) distance of 1.5925 Å, where the extension is due mainly to the presence of a covalently bonded hydrogen. Thus the P(2)-O distances support the assignment of half a covalently bonded hydrogen on average to each O(6) and O(7).

O(5) has the next longest P-O distance after O(6) and O(7). Although O(5) is bonded only to one Ca ion, where O(6) and O(7) and O(8) are all bonded to two, it is the acceptor in the strong "normal" hydrogen bond involving H(1) on O(1), which probably serves to lengthen the P(2)-O(5) bond. The shortest P(2)...O distance is P-O(8), which is the acceptor in the hydrogen bond involving the statistically affected hydrogen H(3) covalently bonded to O(6).

Because on average O(8) enters into only half a hydrogen bond, P(2)...O(8) is not expected to be as long as P(2)...O(5) (the effect of the two Ca ions bonded to O(8) and one Ca ion to O(5) is expected to be subordinate to the effect of hydrogen bonds). Thus, the observed P(2)...O distances are compatible with the environments of the oxygen atoms.

The hydrogen positions

The four hydrogens in the unit cell of $CaHPO_4$ have an unusual distribution over the hydrogen bonding sites. The shortest interphosphate O....O distance, 2.458(2) Å, is between the centrosymmetrically related atoms O(7) and O(7′). Only one of the four hydrogen atoms, H(2), can be placed in this hydrogen bond, and is either on the center of symmetry or disordered about that center. The next shortest interphosphate O....O distance, 2.565(1) Å, is between O(1) and O(5). Two hydrogens, H(1) and H(1′), in general positions, can be accommodated in hydrogen bonds of this type. The fourth hydrogen, H(3), seems to occupy a hydrogen bonding position between O(6) and O(8′), where O(6)...O(8′) = 2.669 Å. This hydrogen can fill only one-half of the two available sites and must, therefore, be disordered. When an idealized position is generated for H(3) according to the rationale given below, H(3) occupies a site (see Fig. 3b) where it also appears to form a very weak bond between O(6) and O(6′), which have a separation of 3.144(2) Å. In this bond, the disorder would be with respect to a center of symmetry analogous to that in the H(2) hydrogen bond. Full occupancy of the H(3) sites would bring pairs of hydrogen atoms improbably close

together, i.e., about 1.45 Å. Thus, it would appear that all the H(3) sites could not be filled even if hydrogen atoms were available.

Because hydrogen positions are imprecisely located by X-ray methods, probable positions of the hydrogen atoms in $CaHPO_4$ were calculated assuming the O-H distance to be 1.00 Å and the P-O-H angle to be 109.5° . The hydrogens were assumed to lie in the same plane as the heavy atoms in the system P-O-H...O. This will give the shortest possible H...O distance, which in general is a realistic approximation. H(3), however, forms a hydrogen bond between two oxygen atoms in the Ca(2) coordination (see Fig. 3b) and its position may lie out of the P(2), O(6), O(8) plane because of repulsion by Ca. The positions of H(3) given in Table 3 lie -0.06 Å, -0.20 Å and 0 Å (assumed), respectively, out of this plane; Ca(2) lies 1.592 Å from the same plane. The Ca(2)...H(3) distance is 2.52 Å for the calculated hydrogen position. Because H(3) is poorly defined in the X-ray refinements, clarification of the effect of Ca(2) on the position of H(3) will have to be made from a neutron diffraction study of $CaHPO_4$.

Discussion

The distance O(7)...O(7′) in the hydrogen bond O(7)-H(2)...O(7′) is 2.458(2) Å, which implies a very strong hydrogen bond. An extensive study at different temperatures of the hydrogen bonds in $CaHPO_4$ by neutron diffraction and spectroscopic methods appears warranted. Whether or not this hydrogen bond and indeed the whole structure is truly or only nominally centrsymmetric is not yet known, although Denne and Jones (1969) give a personal communication from W. G. Perdok that a very weak piezo-electric effect has been found in $CaHPO_4$. In the opinion of the present authors, the R_w factor reported here is close to or at the limit of the data and testing the centrosymmetry of the whole structure by refining in space-group P1 and subsequently applying the ratio test (Hamilton, 1965) would not be worthwhile. The distance O(7)...O(7) reported here is comparable with the O...O separations of 2.459(9) Å in potassium hydrogen malonate, $KOOC \cdot CH_2 \cdot COOH$ (Sime and Speakman, 1970), 2.40 Å in potassium hydrogen chloromaleate, KOOC·CH = CCl·COOH (Ellison and Levy, 1965), 2.437(4) Å in potassium hydrogen maleate, KOOC·CH = CH·COOH (Darlow and Cochran, 1961), and 2.49(2) Å in $HCoO_2$ (Hamilton and Ibers, 1963) where centered hydrogen bonds are probable in all cases.

In the O(6)-H(3)...O(8) hydrogen bond in $CaHPO_4$, the observed O(6)...O(8) distance of 2.669(2) Å is close to halfway between the O(7)...O(7′) distance of 2.458 Å observed here for a very

strong hydrogen bond and the usual non-hydrogen bonded O...O closest inter-ionic approach of ~2.76 Å, and is, therefore, reasonable for a hydrogen bond in which half the hydrogens are statistically absent. This bond is in the edge of the Ca coordination and hence is probably a relatively unfavorable place for a hydrogen atom. Further, the calculated hydrogen position for H(3) (see Fig. 3b) is such that both O(8′) and O(6′) in the adjacent $P(2)O_4$ group may be considered to be acceptors of the hydrogen bond. Thus, the two possible sites for H(3) are only 1.45 Å apart, and it is improbable that both sites would be occupied simultaneously. The maximum rms amplitudes of apparent vibration for O(6) and O(8) are 0.175 Å in each case. In our experience more typical values in the absence of positional disorder are ~0.10 Å. The maximum amplitude of O(8) is more or less along the O(6)...O(8′) vector; that for O(6) is roughly perpendicular to this vector (see Fig. 3b). O(6) and O(8′), therefore, seem to be exhibiting positional disorder depending on the occupancy of the H(3) site, as would be expected because the average O(6)...O(8′) separation of 2.669 Å is too small to be realistic in those cases where there is no H(3) between O(6) and O(8′).

The O(6)...O(8′) separations with and without H(3) intervening can be estimated. When the H(3) site is occupied, O(8′) is expected to be ~(0.175 - 0.100) = ~0.075 Å nearer O(6) than the observed average separation (2.669 Å) of O(6) and O(8′). Similarly, O(6) may be expected to move toward the continuation of the P(2)...O(8) vector. By Pythagoras' rule, the O(6)...O(8) separation when the hydrogen bond is occupied will be approximately $[(2.669 - 0.075)^2 - (0.075)^2]^{\frac{1}{2}} = 2.593$ Å, which indicates a strong hydrogen bond.

When the H(3) site is unoccupied, the O(6)...O(8) separation will be $\sim[(2.669 + 0.075)^2 + (0.075)^2]^{\frac{1}{2}} = 2.745$ Å, which is comparable with the closest O...O non-bonded contact distance of ~2.76 Å usually observed. That O(6)...O(8) are undergoing positional disorder is corroborated by the apparent thermal motion of Ca(2), which is bonded to both O(6) and O(8), and which has apparent thermal amplitudes of 0.138 Å and 0.132 Å toward O(6) and O(8), respectively.

The positional disorder of O(6) inferred above from the thermal parameters indicates that, as expected, O(6) approaches Ca(1) more closely when there is no H(3) attached and vice versa. Ca(1)...O(6) is a short bond for an oxygen covalently bonded to hydrogen (see later in the Discussion). The apparent thermal parameters in the remainder of the $P(2)O_4$ group suggest that this whole group undergoes some displacement depending on the occupancy of the hydrogen sites.

The distance of 1.45 Å between the occupied and unoccupied sites for H(3) is probably too large for a rapid interchange of occupancy to take place. Further, if rapid interchange were taking place, the apparent thermal parameters of O(6) and O(8) might be expected to be more isotropic since, because of their greater mass and their fairly rigid attachment to the PO_4 group, they would be expected to move more slowly than H(3). Indeed, because of the changing π character of the P(2)-O(6) bond depending on whether or not H(3) is covalently bonded to O(6), the greatest apparent thermal motion of O(6) under these circumstances might be expected to be along the P(2)-O(6) bond. Actually O(6) has essentially its smallest amplitude of apparent thermal motion (0.087 Å) along this direction. Thus, H(3) seems to be

relatively firmly attached to O(6), and probably forms a hydrogen bond which is abnormal only in its statistical disorder.

The relationship of $CaHPO_4$ to some other calcium phosphates and related compounds is discussed next. The structures of $CaHPO_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2 \cdot H_2O$ contain corrugated sheets made up of $(CaHPO_4)^\circ$ and $(CaH_2PO_4)^+$ chains, respectively. In $CaSO_4 \cdot 2H_2O$, there are corresponding $CaSO_4$ chains and sheets. In $Ca(H_2PO_4)_2 \cdot H_2O$, the $Ca(H_2PO_4)^+$ sheets are separated by $H_2PO_4^-$ ions and water molecules. Sheets similar to those in the above compounds may also be present in $Ca_2(NH_4)H_7(PO_4)_4 \cdot 2H_2O$, $Ca_2KH_7(PO_4)_4 \cdot 2H_2O$, and $CaCl(H_2PO_4) \cdot H_2O$ (Brown, Smith, Lehr and Frazier, 1958). The widespread occurrence of the corrugated sheet feature speaks for its stability.

The structures of $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ are closely related if allowance is made for the water molecules; corrugated sheets in $CaHPO_4$ may be imagined parallel to several planes, e.g., (101), $(10\bar{1})$ and (001), with the Ca-PO_4 chains running parallel to [010] (see Fig. 1). It is of interest to compare the sheets in $CaHPO_4$, $CaSO_4$, $CaHPO_4 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, and $Ca(H_2PO_4)_2 \cdot H_2O$. This comparison may be done in terms of the Ca coordinations in the five compounds (Fig. 2a through 2f). In $Ca(H_2PO_4)_2 \cdot 2H_2O$ (Fig. 2f), the shortest Ca...O bonds (2.3 , 2.326 Å) are between chains in the same layer; the next shortest (2.393, 2.475 Å) are from the surface of the layer to the interlayer $H_2O/H_2PO_4^-$ network; the next longest bonds (2.521, 2.538 Å) are to PO_4 oxygens which are in the same chain as the Ca ion but which have no covalently bonded hydrogen atoms; the longest (2.626, 2.628 Å)

are to the oxygens in the same chain which have covalently bonded hydrogens. The pattern is the same in $CaSO_4$ (Fig. 2c), $CaHPO_4 \cdot 2H_2O$ (Fig. 2d), and $CaSO_4 \cdot 2H_2O$ (Fig. 2e) though actual distances are a little different.

For Ca(1) in $CaHPO_4$, Ca(1)...O(7) is the longest bond, and Ca(1) is so far away from O(5) (3.427 Å) that they are not considered to be bonded. This is to be expected from the above descriptions, because these atoms are in the same chain and O(5) and O(7) are covalently bonded to hydrogens. The other Ca...O distances do not follow the previous pattern, however. In particular, the Ca(1)...O(6) distance, which is within the chain and where half of the O(6) atoms in the structure are considered to be covalently bonded to hydrogen, is relatively short, 2.451 Å. (However, as was remarked earlier, the position of O(6) is believed to be an average of two slightly different positions depending on the occupancy of the H(3) site.) In the case of Ca(2) in $CaHPO_4$, O(1), which is covalently bonded to hydrogen and is within the chain, is so far away that it is not considered to be bonded to Ca(2); on the other hand, the other member, O(3), of the PO_4 edge O(1,3) has the shortest Ca(2)...O bond. $CaSO_4$ conforms to the general pattern; the formally analogous compound $CaHPO_4$ does not, probably because of the deforming power of the hydrogen bonds, two of which are very strong, and partly because of the averaged effects of hydrogen disorder.

Much of the disruptive effect on the Ca-PO_4 coordinations can be traced to H(1) which, in forming the bond O(1)-H(11)...O(5) apparently breaks up two edge sharing by pulling O(1) away from Ca(2) and O(5) from Ca(1).

Two other possible factors in the non-conformity of $CaHPO_4$ are Ca...H repulsions and the size of the oxygen coordination polyhedron round Ca. The distances Ca...O where O is coordinated to hydrogen are (i) 2.390 Å and 2.427 Å to the water oxygens in $CaHPO_4 \cdot 2H_2O$, (ii) ~2.34 Å to the water oxygens in $CaSO_4 \cdot 2H_2O$, and (iii) 2.476 Å to the water oxygen in $Ca(H_2PO_4)_2 \cdot H_2O$. These Ca...O distances are all quite short, and involve repulsion of two hydrogens per oxygen atom. This suggests that Ca...H repulsions are not the main force in the distortion of $CaHPO_4$. The mean O...O separation in an edge of the SO_4 group in $CaSO_4$ is 2.43 Å. In the PO_4 groups in $CaHPO_4$, the average O...O separation is 2.509 Å. Thus, although the $CaSO_4$ structure may not be stable for $CaHPO_4$, a change of ~0.075 Å in O...O distances should not be drastic, and the difference in coordination polyhedron size is probably not structure-determining. We are then left with the reasonable conclusion that the O-H...O hydrogen bonds distort the $CaHPO_4$ structure.

The deforming power of hydrogen bonds in calcium phosphates is of interest if PO_4^{3-} groups in the structures become HPO_4^{2-} or $H_2PO_4^-$ groups to restore electroneutrality if some Ca^{2+} ions are missing. In cases such as these, the structure probably undergoes some local distortion, and in extreme cases, may even be so distorted that it remains amorphous.

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References

Atoji, M. and Rundle, R. E. (1958). J. Chem. Phys. 29, 1306.

Beevers, C. A. (1958). Acta Cryst. 11, 273.

Brown, W. E., Smith, J. P., Lehr, J. R. and Frazier, A. W. (1958). J. Phys. Chem. 62, 625.

Cheng, G. C. H. and Zussmann, J. (1963). Acta Cryst. 16, 767.

Cromer, D. T. (1965). Acta Cryst. 18, 17.

Cromer, D. T. and Mann, J. B. (1968). Acta Cryst. A24, 321.

Cruickshank, D. W. J. (1961). J. Chem. Soc., 5486.

Curry, N. A., Denne, W. A. and Jones, D. W. (1968). Bull. Soc. Chim. France, 1748.

Curry, N. A. and Jones, D. W. (1970). Private communication.

Darlow, S. F. and Cochran, W. (1961). Acta Cryst. 14, 1250.

Denne, W. A. and Jones, D. W. (1969). Abstract XII -78, VIII International Congress of Crystallography, Stony Brook, New York, August, 1969.

de Schulten, M. A. (1901). Bull. Soc. Min. 24, 323.

Dickens, B. and Bowen, J. S. (1971a). J. Res. Nat. Bur. Stands. 75A, 27.

Dickens, B. and Bowen, J. S. (1971b). Acta Cryst., in press.

Egan, E. P. and Wakefield, Z. T. (1964). J. Chem. Eng. Data 9, 541.

Ellison, R. D. and Levy, H. A. (1965). Acta Cryst. 19, 260.

Hamilton, W. C. (1965). Acta Cryst. 18, 502.

Hamilton, W. C. and Ibers, J. A. (1963). Acta Cryst. 16. 1209.

Hohne, E. (1962). Monat. Deut. Akad. Wiss. Berlin, 4, 72.

Jones, D. W. and Cruickshank, D. W. J. (1961). Z. Krist. 116, 101.

Jones, D. W. and Smith, J. A. S. (1962). J. Chem. Soc., 1414.

MacLennan, G. and Beevers, C. A. (1955). Acta Cryst. 8, 579.

MacLennan, G. and Beevers, C. A. (1956). Acta Cryst. 9, 187.

Pauling, L. (1960). The Nature of the Chemical Bond, 3rd Edition, p. 559, Ithaca, New York: Cornell University Press.

Perloff, A. (1971). Private communication.

Sime, J. G. and Speakman, J. C. (1970). J. Chem. Soc., 1919.

Zachariasen, W. H. (1967). Acta Cryst. 23, 558.

Table 1 Atomic Parameters in $CaHPO_4$

Atom	x	y	z	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca(1)	.29479(4)	.43386(4)	.27252(4)	.757(7)	1.198(8)	1.067(7)	-.002(6)	.145(6)	-.263(6)
Ca(2)	.17564(4)	.83738(3)	.66528(4)	1.194(8)	.586(7)	1.010(8)	-.090(5)	-.047(6)	.146(5)
P(1)	.20800(4)	.37900(4)	.72135(4)	.560(8)	.443(8)	.638(8)	-.042(6)	.098(6)	.047(6)
P(2)	.29581(4)	.94245(4)	.20824(4)	.851(9)	.732(9)	.689(9)	.171(7)	.092(7)	.048(7)
O(1)	.3226(1)	.3325(1)	.9380(1)	1.04(3)	1.23(3)	.66(2)	.23(2)	.09(2)	.27(2)
O(2)	.3518(1)	.4924(1)	.6332(1)	.74(3)	.91(3)	.89(3)	-.16(2)	.22(2)	.25(2)
O(3)	.1387(1)	.1810(1)	.5958(1)	1.09(3)	.49(2)	1.07(3)	-.13(2)	.05(2)	-.14(2)
O(4)	.0398(1)	.5237(1)	.7459(1)	.71(3)	.76(3)	1.36(3)	.17(2)	.27(2)	.02(2)
O(5)	.3329(1)	.8363(1)	.0155(1)	.99(3)	1.60(3)	.88(3)	.33(2)	.10(2)	-.31(2)
O(6)	.4592(1)	.1024(2)	.3019(2)	.96(3)	1.40(3)	1.69(3)	-.41(2)	-.09(2)	-.54(3)
O(7)	.0995(1)	.0660(1)	.1639(1)	.91(3)	1.35(3)	.83(2)	.51(2)	.02(2)	.03(2)
O(8)	.2874(2)	.7896(2)	.3514(2)	2.24(4)	1.24(3)	1.64(3)	.62(3)	.96(3)	.86(3)

The figures in parentheses are standard deviations calculated in the final least squares refinement.

* Thermal parameters have the form $\exp(-1/4(\underline{a}^{*2}\underline{B}_{11}\underline{h}^2 + \underline{b}^{*2}\underline{B}_{22}\underline{k}^2 + \underline{c}^{*2}\underline{B}_{33}\underline{\ell}^2 + 2\underline{a}^*\underline{b}^*\underline{B}_{12}\underline{hk} + 2\underline{a}^*\underline{c}^*\underline{B}_{13}\underline{h\ell} + 2\underline{b}^*\underline{c}^*\underline{B}_{23}\underline{k\ell}))$.

Table 2

Calculated and observed structure factors for $CaHPO_4$

Table 2 (continued)

-4,K,-3

1	64	-58
2	263	257
3	294	297
4	120	-121
5	49	43
6	143	-147
7	108	108
8	88	87
9	45	48
10	96	-95

-4,K,-2

-10	25	28
-9	115	-116
-8	59	59
-7	226	230
-6	16	-8
-5	188	190
-4	313	-315
-3	106	-99
-2	154	-150
-1	12	4
0	94	-96
1	22	18
2	399	-402
3	127	-133
4	170	173
5	33	28
6	354	358
7	32	17
8	68	-64
9	85	84
10	71	-72
11	146	138

-4,K,-1

-11	67	-71
-10	35	34
-9	138	139
-8	241	245
-7	18	-18
-6	234	226
-5	319	-318
-4	243	234
-3	16	-5
-2	171	166
-1	28	25
0	534	-544
1	155	-148
2	258	-262
3	101	-106
4	209	209
5	188	-192
6	16	10
7	56	-59
8	10	-3
9	66	64
10	204	203
11	50	49

-4,K,0

-11	150	152
-10	87	-88
-9	98	94
-8	68	-70
-7	154	-154
-6	61	60
-5	98	93
-4	206	197
-3	196	188
-2	198	195
-1	142	-149
0	50	49
1	142	-139
2	34	36
3	109	98
4	251	-245
5	13	-7
6	390	-398
7	94	94
8	93	92
9	11	2
10	85	87
11	158	-157

-4,K,1

-11	27	-23
-10	82	-90
-9	191	-194
-8	97	-98
-7	140	138
-6	203	-200
-5	313	307
-4	409	-394
-3	69	-81
-2	130	133
-1	11	-1
0	558	579
1	87	83
2	16	-6
3	116	-118
4	80	83
5	215	220
6	169	166
7	51	-52
8	191	-191
9	167	-164
10	128	-129
11	67	68

-4,K,2

-11	159	-165
-10	123	127
-9	10*	8
-8	143	143
-7	28	-22
-6	165	159
-5	190	193
-4	509	-512
-3	200	203
-2	129	130
-1	280	285
0	542	543
1	119	-117
2	99	103
3	131	-130
4	99	-90
5	59	57
6	54	-53
7	131	-130
8	71	-72
9	59	57
10	54	-53
11	51	50

-4,K,3

-11	172	174
-10	30	31
-9	104	98
-8	26	-24
-7	166	-163
-6	173	174
-5	157	-153
-4	206	195
-3	165	-167
-2	183	-182
-1	182	179
0	300	-313
1	127	133
2	93	-99
3	11	-9
4	34	-30
5	54	48
6	159	-157
7	127	126
8	134	136
9	58	58
10	134	133

-4,K,4

-11	58	55
-10	119	-122
-9	46	-44
-8	59	60
-7	143	144
-6	145	143
-5	206	208
-4	67	66
-3	61	-58
-2	177	189
-1	192	-203
0	346	358
1	352	-375
2	118	-121
3	380	-402
4	308	-322
5	192	199

-4,K,5

-11	194	-190
-10	38	32
-9	40	-36
-8	79	80
-7	216	221
-6	241	-238
-5	113	111
-4	93	-94
-3	253	252
-2	354	362
-1	108	116
0	144	-156
1	244	-257
2	47	-48
3	64	65
4	154	158
5	116	-121
6	91	-90
7	218	-212
8	80	80
9	100	96
10	47	-43

-4,K,6

-10	88	86
-9	17	-18
-8	159	-165
-7	134	-134
-6	19	-18
-5	52	-46
-4	124	121
-3	64	65
-2	263	-272
-1	305	321
0	159	-170
1	378	400
2	58	59
3	41	34
4	101	107
5	87	-88
6	35	33
7	37	-34
8	8*	-2
9	12	9

-4,K,7

-10	81	-86
-9	15	-18
-8	65	63
-7	77	-72
-6	140	140
-5	300	-302
-4	21	-20
-3	206	-211
-2	74	74
-1	7*	-6
0	111	119
1	54	-56
-1	220	-224
0	31	21
1	260	261
2	271	277
3	78	79
4	97	-96
5	8*	4
6	83	84
7	255	257
8	10*	-13
9	42	41

-4,K,8

-9	60	58
-8	72	74
-7	146	144
-6	108	-109
-5	14	6
-4	173	-177
-3	21	17
-2	127	129
-1	147	-150
0	38	38
1	348	-360
2	44	-40
3	114	113
4	45	43
5	168	171
6	47	-49
7	45	-47
8	20	-17

-4,K,9

-9	24	24
-8	102	-103
-7	41	42
-6	49	-50
-5	199	202
-4	107	103
-3	84	80
-2	103	-105
-1	25	24
0	42	-46
1	95	97
2	21	-20
3	106	-103
4	36	-37
5	214	-216
6	53	47
7	59	-57

-4,K,10

7	118	-117
8	121	122
9	42	-37
10	111	112

-5,K,-3

7	10*	-5
8	86	-85
9	42	-37
10	111	112

-5,K,-2

-9	89	-94
-8	94	-90
-7	9*	12
-6	8*	-5
-5	136	136
-4	131	131
-3	119	-117
-2	147	146
-1	25	-27
0	73	70
1	487	502
2	61	-60
3	216	226
4	343	-350
5	153	-154
6	75	-75
7	35	-31
8	55	54

-5,K,-1

9	136	-138
10	104	-104

-5,K,0

-11	43	-46
-10	49	52
-9	16	10
-8	143	147
-7	13	10
-6	43	-42
-5	150	-151
-4	98	-93
-3	162	-165
-2	42	38
-1	41	-45
0	10	6
1	51	50
2	271	-271
3	242	252
4	53	-53
5	110	112
6	168	168
7	172	-173
8	129	131
9	51	-50
10	70	69

-5,K,5

-10	15	14
-9	234	235
-8	100	-98
-7	153	150
-6	126	-120
-5	29	-12
-4	268	269
-3	95	100
-2	113	108
-1	208	-212
0	328	-342
1	110	-107
2	146	-156
3	90	95
4	117	-121
5	68	-65
6	140	-142
7	107	108
8	10*	2
9	247	238

-5,K,6

-10	24	-22
-9	65	-58
-8	86	-85
-7	24	-14
-6	250	251
-5	176	175
-4	80	90
-3	114	120
-2	178	-180
-1	27	-8
0	117	120
1	171	179
2	182	191
3	294	-302
4	50	-50
5	126	-132
6	46	-42
7	135	138
8	54	-52
9	26	27

-5,K,7

-10	36	-37
-9	80	-75
-8	159	163
-7	95	-94
-6	10	0
-5	54	-55
-4	188	-188
-3	172	172
-2	21	22
-1	132	132
0	114	118
1	7*	-4
2	21	-22
3	130	131
4	69	67
5	22	16
6	29	30
7	210	-208
8	9*	6

-5,K,8

-9	69	61
-8	69	-65
-7	66	-70
-6	181	-185
-5	107	-105
-4	43	41
-3	58	-57
-2	118	117
-1	150	-148
0	69	-70
1	194	200
2	28	-27
3	307	318
4	19	19
5	16	-8
6	27	29
7	65	-64

-5,K,9

-8	113	-113
-7	23	20
-6	54	54
-5	12	-1
-4	33	29
-3	156	-152
-2	62	-62
-1	117	-115
0	11	1
1	12	-4
2	79	78
3	54	-54
4	43	37
5	10*	-5
6	10*	-5

-5,K,10

-11	79	78
-10	20	13
-9	231	-229
-8	46	-47
-7	202	-195
-6	151	147
-5	37	44
-4	198	-198
-3	36	34
-2	347	-352
-1	111	110
0	280	289
1	25	17
2	451	474
3	27	-30
4	80	85
5	30	-32
6	115	114
7	49	-48
8	85	86
9	163	-166
10	100	-101

-6,K,-3

-7	31	29
-6	47	48
-5	46	46
-4	131	-131
-3	157	153
-2	55	-53
-1	78	79
0	23	-21
1	164	-160
2	44	-44
3	112	-112
4	67	58
5	16	18

-6,K,-2

-6	26	-29
-5	60	61
-4	86	80
-3	126	121
-2	104	100
-1	55	-57
0	55	-53
1	47	45
2	47	-43
3	59	59
4	77	-67

-6,K,-1

-8	122	-125
-7	101	103
-6	105	-106
-5	192	-193
-4	6*	6
-3	274	-271
-2	350	355
-1	228	233
0	244	250
1	11	0
2	18	19
3	137	-140
4	227	229
5	108	110
6	93	-96
7	30	27
8	249	-255
9	40	39
10	27	-28

-6,K,0

-9	14	7
-8	122	-125
-7	101	103
-6	105	-106
-5	192	-193
-4	6*	6
-3	274	-271
-2	350	355
-1	228	233
0	244	250
1	11	0
2	18	19
3	137	-140
4	227	229
5	108	110
6	93	-96
7	30	27
8	249	-255
9	40	39
10	27	-28

-6,K,1

-9	80	87
-8	38	39
-7	191	-193
-6	146	-147
-5	27	28
-4	46	46
-3	323	330
-2	352	-361
-1	178	-179
0	331	-341
1	181	-193
2	433	448
3	101	-101
4	180	182
5	7*	1
6	53	-54
7	147	147
8	93	96
9	98	100
10	23	22

-6,K,2

-9	65	-58
-8	86	-85
-7	24	-14
-6	250	251
-5	176	175
-4	80	90
-3	114	120
-2	178	-180
-1	27	-8
0	117	120
1	171	179
2	182	191
3	294	-302
4	50	-50
5	126	-132
6	46	-42
7	135	138
8	54	-52
9	26	27

-6,K,3

-9	69	61
-8	69	-65
-7	66	-70
-6	181	-185
-5	107	-105
-4	43	41
-3	58	-57
-2	118	117
-1	150	-148
0	69	-70
1	194	200
2	28	-27
3	307	318
4	19	19
5	16	-8
6	27	29
7	65	-64

-6,K,4

-8	76	-80
-7	32	32
-6	200	-201
-5	213	215
-4	138	-135
-3	55	-54
-2	184	-183
-1	240	-242
0	86	88
1	31	-24
2	160	157
3	14	11
4	29	-29
5	23	-20
6	102	107
7	65	62
8	162	160
9	71	68

-6,K,5

-9	99	-100
-8	44	42
-7	133	134
-6	127	130
-5	20	-13
-4	12	4
-3	77	-74
-2	84	-86
-1	249	250
0	139	-142
1	78	81
2	240	-245
3	250	-250
4	30	29
5	86	-85
6	246	252
7	51	-47
8	19	-11
9	26	-24

-6,K,6

-9	65	61
-8	38	37
-7	48	-47
-6	184	187
-5	185	-192
-4	205	202
-3	118	117
-2	86	85
-1	273	278
0	111	-112
1	29	-25
2	102	-104
3	70	74
4	123	-123
5	86	89
6	256	-258
7	78	-73
8	131	-130
9	40	-38
10	89	90

-6,K,7

-10	10*	-2
-9	8*	3
-8	121	-125
-7	116	-117
-6	92	-91
-5	119	115
-4	49	47
-3	51	53
-2	74	74
-1	210	-217
0	470	493
1	50	-49
2	336	336
3	74	76
4	239	-245
5	19	-22
6	184	-185
7	8*	0
8	52	51
9	14	-15
10	72	-72

-6,K,8

-10	62	-60
-9	9*	-7
-8	107	109
-7	56	48
-6	123	122
-5	30	29
-4	106	-102
-3	132	-133
-2	14	-11
-1	195	-203
0	140	146
1	105	-107
2	107	-107
3	84	-88
4	260	-267
5	212	216
6	18	-14
7	228	228
8	11*	13

-6,K,9

-9	24	22
-8	63	64
-7	151	153
-6	130	-130
-5	160	168
-4	56	-57
-3	80	80
-2	218	220
-1	117	-118
0	42	-46
1	234	-243
2	91	-95
3	63	-64
4	88	89
5	91	-92
6	13	-7
7	46	-47
8	10*	5

-6,K,10

-9	45	-40
-8	85	88
-7	87	-85
-6	31	31
-5	81	86
-4	179	182
-3	32	-24
-2	123	-121
-1	82	84
0	66	-71
1	261	267
2	91	89
3	116	-119
4	71	76
5	204	-207
6	80	76
7	50	-50

-7,K,-6

-8	10*	0
-7	30	-34
-6	49	47
-5	141	-138
-4	73	-68
-3	46	-43
-2	47	-49
-1	177	174
0	32	31
1	170	176
2	42	40
3	69	67
4	83	-83
5	125	129
6	63	-60

-7,K,-5

-7	10*	-4
-6	104	-101
-5	17	-12
-4	81	-80
-3	54	-51
-2	100	99
-1	106	-101
0	88	87
1	135	-133
2	34	33
3	79	77
4	9*	5
5	130	130

-7,K,-4

-6	35	-37
-5	118	112
-4	100	100
-3	40	-41
-2	75	-67
-1	126	-122
0	45	-44
1	18	12
2	63	55
3	172	-106

-7,K,-3

-9	98	95
-8	107	-109
-7	218	213
-6	74	-70
-5	27	-24
-4	7*	2
-3	87	-91
-2	279	285
-1	174	182
0	113	115
1	30	34
2	177	-178
3	72	-70
4	117	112
5	54	53
6	113	-115
7	53	-53
8	282	-279
9	36	30

-7,K,-2

-10	47	44
-9	80	85
-8	9*	3
-7	167	-165
-6	194	-193
-5	53	-50
-4	85	-87
-3	296	302
-2	117	-120
-1	33	16
0	102	-102
1	51	-52
2	369	370
3	24	-26
4	204	201
5	70	-66
6	104	-101
7	92	88
8	10*	-11
9	53	50

-7,K,-1

-10	72	72
-9	193	-203
-8	126	126
-7	117	-110
-6	155	152
-5	53	41
-4	193	-194
-3	138	-142
-2	167	-165
-1	52	-53
0	47	-53
1	17	8
2	128	-126
3	87	85
4	20	19
5	138	134
6	187	186
7	2	0
8	182	176
9	82	-80

-7,K,0

-10	24	-21
-9	93	90
-8	75	72
-7	190	187
-6	26	-22
-5	51	-49
-4	56	56
-3	282	-288
-2	190	189
-1	104	-106
0	106	-110
1	21	17
2	341	-350
3	70	68
4	15	13
5	158	153
6	69	64
7	55	-52
8	48	-47
9	9*	-6

-7,K,1

-9	185	-185
-8	60	-62
-7	102	-98
-6	79	81
-5	158	157
-4	139	-134
-3	179	170
-2	153	-150
-1	321	325
0	166	168
1	48	49
2	106	108
3	168	-167
4	46	-45
5	11	0
6	38	-39
7	17	-11
8	33	-33

-7,K,2

-8	85	-89
-7	88	86
-6	86	87
-5	118	114
-4	34	-34
-3	19	12
-2	201	-201
-1	59	58
0	36	15
1	133	-133
2	54	53
3	232	-233
4	24	-25
5	21	17
6	14	2

-7,K,3

-7	13	9
-6	12	14
-5	15	7
-4	105	-104
-3	186	180
-2	17	-12
-1	146	147
0	22	19
1	84	-84
2	71	-69
3	15	-9
4	9*	6
5	38	40

-7,K,10

-6	33	-30
-5	83	-80
-4	97	99
-3	46	-40
-2	126	125
-1	24	-25
0	31	28
1	126	122
2	18	-14
3	172	173
4	56	-44

-7,K,11

-5	35	-31
-4	12	3
-3	105	-102
-2	19	-20
-1	18	17
0	82	79
1	35	38
2	34	37

-8,K,-7

-4	83	-83
-3	58	58
-2	74	77
-1	156	-158
0	14	8
1	193	-195
2	14	2
3	93	94
4	29	24
5	90	88

-8,K,-5

-5	185	190
-4	48	49
-3	29	-27
-2	87	-85
-1	170	-170
0	35	-32
1	39	39
2	18	16
3	122	-122
4	13	5
5	230	-231
6	103	101

-8,K,-4

-6	116	110
-5	57	-58
-4	53	58
-3	8*	0
-2	15	-17
-1	209	215
0	118	-119
1	166	171
2	146	-148
3	123	-125
4	37	-39
5	74	-75
6	44	38
7	32	29

-8,K,-3

-7	67	-70
-6	29	-30
-5	72	-80
-4	27	19
-3	70	69
-2	118	122
-1	18	20
0	16	17
1	55	-60
2	58	56
3	164	166
4	16	14
5	175	176
6	207	-206
7	9*	5

-8,K,-2

-8	59	-58
-7	97	97

-8,K,-1

-8	30	33
-7	126	128
-6	17	-14
-5	37	-27
-4	126	-126
-3	121	-120
-2	78	-82
-1	152	157
0	128	-132
1	128	128
2	95	-96
3	145	-146
4	115	117
5	92	-91
6	196	194
7	9*	-2
8	16	8

-8,K,0

-9	104	105
-8	34	36
-7	60	-55
-6	100	103
-5	108	-110
-4	222	226
-3	105	111
-2	123	124
-1	120	126
0	283	-290
1	98	-99
2	112	-112
3	63	-61
4	30	-29
5	29	-27
6	129	-128
7	32	-33
8	79	77

-8,K,1

-9	24	-19
-8	43	-42
-7	50	-53
-6	27	21
-5	178	176
-4	170	173
-3	90	92
-2	30	28
-1	206	-210
0	132	139
1	73	-76
2	147	148
3	47	49
4	285	-287
5	34	34
6	251	-250
7	54	52
8	44	44
9	22	10

-8,K,2

-9	123	-121
-8	49	-45
-7	147	148
-6	119	-121
-5	96	90
-4	198	-200
-3	70	-71
-2	36	36
-1	77	78
0	193	196
1	79	78
2	54	51
3	37	-31
4	33	29
5	12	4
6	117	115
7	32	-31
8	96	-94

-8,K,3

-9	78	76
-8	29	27
-7	100	-97
-6	72	-70
-5	258	-260
-4	77	74
-3	17	-11
-2	52	-55
-1	92	90
0	269	-273
1	18	14
2	94	93
3	80	79
4	293	298
5	85	-87
6	127	125
7	79	-75
8	97	94

-8,K,4

-9	68	69
-8	37	-30
-7	88	-87
-6	133	130
-5	37	-36
-4	115	113
-3	25	-25
-2	228	-233
-1	125	-128
0	104	-103
1	21	-19
2	53	50
3	102	101
4	133	-129
5	130	128
6	75	-77
7	93	89
8	106	105

-8,K,5

-8	9*	4
-7	156	153

-8,K,6

-8	8*	-1
-5	163	162
-4	116	-117
-3	36	34
-2	60	57
-1	86	-87
0	211	211
1	114	-112
2	53	-50
3	29	-23
4	232	-232
5	57	57
6	63	-58
7	31	26
8	70	-65

-8,K,7

-8	25	22
-7	20	-9
-6	100	-96
-5	96	-89
-4	79	76
-3	149	149
-2	205	208
-1	82	83
0	21	-20
1	58	-56
2	11	11
3

Table 2 (continued)

-9,K,-3			-5 8* 4			5 25 24			-3 178 -181			-5 28 -22			-1 133 -138			4 71 -65			3 41 -40			3 28 26			-1 18 20			-3 172 174			3 38 -33			-12,K,2		
			-4 107 -108			6 13 9			-2 126 125			-4 33 -32			0 75 -76			5 9* -6			4 169 -162			4 43 -37			0 30 -28			-2 138 -137			4 27 24					
1 23 21			-3 172 180			7 17 12			-1 111 -113			-3 34 51			1 22 23			6 61 -58			5 63 61			5 110 103			1 167 -159			-1 7* -6					-3 22 22
2 54 -54			-2 247 -255			8 152 -145			0 43 -41			-2 97 96			2 22 -21						6 108 -101						2 85 82			0 55 -52			-11,K,6		-2 100 96
3 67 68			-1 29 -30						1 96 92			-1 57 56			3 25 22			-10,K,1						-10,K,7			3 108 -107			1 40 -38					-1 126 -127
4 148 -146			0 52 -52			-9,K,3			2 213 -211			0 12 -2			4 13 6						-10,K,4									2 224 223			-5 29 29			0 216 215
5 33 -34			1 28 -28						3 131 129			1 78 78			5 46 -43			-7 79 84						-6 20 20			-11,K,-1			3 21 23			-4 61 -62		1 50 -47
6 10* -8			2 196 198			-8 37 -34			4 20 -15			2 96 -95						-6 13 -1			-7 130 133			-5 45 45						4 56 53			-3 26 23		2 104 95
			3 38 34			-7 66 -68			5 106 105			3 64 61			-10,K,-2			-5 24 -27			-6 42 -46			-4 56 -56			-4 14 -1			5 57 -52			-2 76 -73		3 45 -40
-9,K,-2			4 20 16			-6 43 -48			6 109 108			4 30 -21						-4 145 -148			-5 134 132			-3 75 -75			-3 71 76						-1 53 52		
			5 56 -55			-5 14 9			7 15 5			5 12 1			-5 104 -108			-3 93 -98			-4 110 -110			-2 79 74			-2 132 -130			-11,K,3			0 150 147		-12,K,3
-7 40 36			6 39 37			-4 8* -2			-9,K,6			-9,K,9			-4 14 2			-2 17 -5			-3 38 -35			-1 117 -113			-1 81 -85						1 42 37		
-6 18 11			7 17 -15			-3 194 197									-3 64 -62			-1 109 109			-2 115 113			0 128 124			0 141 -144			-6 72 72			2 84 82		-3 10* 2
-5 11 0			8 116 111			-2 71 -72									-2 34 -35			0 37 -36			-1 18 19			1 196 -181			1 26 25			-5 8* 1			3 15 -9		-2 10* 7
-4 131 133						-1 18 -18			-8 50 -47			-5 33 -33			-1 109 108			1 84 85			0 137 136			2 27 -17			2 18 9			-4 29 -30			4 13 8		-1 106 106
-3 156 -162			-9,K,1			0 39 38			-7 59 57			-6 62 62			0 121 -122			2 67 -66			1 43 -41			3 63 -58			3 80 80			-3 138 -135					0 39 39
-2 128 133						1 66 -63			-6 9* 0			-3 126 -119			1 31 30			3 37 -37			2 18 -18			4 63 -62			4 33 -35			-2 61 -60			-11,K,7		1 48 47
-1 13 7			-8 19 19			2 319 318			-5 10* 7			-2 32 33			2 129 -128			4 184 183			3 87 -84									-1 57 -57					2 54 -47
0 122 122			-7 35 34			3 54 -55			-4 120 120			-1 67 -69			3 67 -71			5 40 -39			4 55 51			-10,K,8			-11,K,0			0 9* 2			-4 18 -17		3 65 -58
1 172 173			-6 111 115			4 112 106			-3 17 -13			0 100 -100			4 69 66			6 154 149			5 13 -6									1 43 41			-3 27 -23		
2 72 -75			-5 81 85			5 140 -134			-2 52 54			1 120 114			5 55 -55						6 64 61			-5 79 75			-5 18 19			2 80 -80			-2 86 79		
3 70 67			-4 18 -17			6 90 -89			-1 116 -117			2 21 -18						-7 92 -87			-10,K,5			-4 11* -13			-4 93 96			3 62 55			-1 9* 0		-12,K,4
4 167 -165			-3 78 -79			7 41 40			0 92 -91			3 150 144			-10,K,-1			-6 71 74			-7 46 -46			-3 99 94			-3 134 -138			4 49 -47			0 26 -23		-3 22 19
5 9* 9			-2 40 -37						1 74 -71			4 10* -1						-7 92 -87			-5 173 -176			-2 32 30			-2 93 96			5 17 11			1 106 96		-2 116 -113
6 10* -2			-1 7* -2			-9,K,4			2 64 60									-6 71 74			-4 95 95			-1 62 63			-1 20 -18						2 85 -83		-1 52 52
7 41 40			0 27 -28						3 54 -53			-9,K,10						-7 96 -98			-5 123 -125			1 57 -53			1 134 135			-11,K,4			3 175 157		0 166 -161
			1 101 101			-8 7* -8			4 11 8						-5 114 -117			-4 69 66			-4 12 2			2 70 -72			2 92 -89						-11,K,8		1 86 79
-9,K,-1			2 329 -332			-7 87 -86			5 71 -71			-4 13 -5			-3 60 62			-3 19 -18			-4 12 2			3 43 39			3 34 33			-6 33 -33					2 40 -37
			3 74 74			-6 30 30			6 140 -135			-3 110 -105			-2 155 161			-2 19 -13			-3 43 39									-5 51 -49					
-7 101 97			4 268 -270			-5 85 84						-2 110 -106			-1 33 25			-1 46 47			-2 16 -10			-10,K,9			4 138 -132			-4 84 79			-11,K,8		-12,K,5
-6 38 -39			5 20 16			-4 255 -259			-9,K,7			-1 47 -45			0 69 71			0 216 -218			-1 195 196						5 48 -45			-3 74 -70			-2 19 16		
-5 106 -108			6 82 82			-3 9* 3						0 53 48			1 99 -102			1 28 -32			0 164 -163									-2 76 76			-1 78 -74		-3 72 -68
-4 84 -86			7 20 18			-2 204 -206			-7 23 -22			1 46 -40			2 9* -2			2 100 -95			1 167 148			-4 101 103			-11,K,1			-1 34 -33			0 64 -66		-2 16 -17
-3 51 -52			8 125 122			-1 118 119			-6 93 93			2 125 118			3 51 50			3 8* -4			2 24 23			-3 29 24						0 90 -89			1 58 -54		-1 148 -148
-2 36 32						0 128 127			-5 173 173						4 16 -10			4 71 70			3 86 84			-2 75 -74			-5 57 -60			1 26 -26					0 63 60
-1 117 121			-9,K,2			1 181 177			-4 67 -63			-10,K,-4			5 44 44			5 21 16			4 179 174			-1 118 111			-4 45 43			2 144 -144			-12,K,0		1 47 -42
0 151 152						2 18 -18			-3 93 90						6 157 -154			6 43 -41			5 44 -41			-3 20 17			3 17 17						2 11* 11
1 112 -114			-8 32 -33			3 66 65			-2 114 -114			-3 60 60			-10,K,0			-10,K,3			6 20 -17			1 113 106			-2 121 120			4 72 -63			-1 122 122		
2 150 150			-7 129 127			4 17 -15			-1 101 99			-2 111 115												2 14 4			-1 117 117			5 69 66			0 120 -122		-12,K,6
3 109 -108			-6 74 74			5 42 40			0 148 144			-1 78 -80									-10,K,6						0 66 66						1 47 45		
4 241 236			-5 44 -42			6 142 140			1 20 -17			0 80 80			-6 159 -164			-7 11* 2						-11,K,-3			1 44 -40			-11,K,5					-2 73 68
5 100 98			-4 174 178			7 37 -30			2 80 77			1 183 -186			-5 179 186			-6 23 22			-6 70 65						2 62 60						-12,K,1		-1 47 -44
6 27 22			-3 126 -129						3 260 -248			2 36 35			-4 56 -56			-5 115 119			-5 107 -101			-1 38 -36			3 95 -89			-5 41 29					0 108 103
7 30 -28			-2 225 229			-9,K,5			4 39 -39			3 106 103			-3 104 104			-4 62 64			-4 57 59			0 71 69			4 45 47			-4 58 57			-3 26 28		
			-1 54 -53						5 110 -107						-2 38 36			-3 39 43			-3 70 -70			1 106 103			5 36 36			-3 153 153			-2 16 -11		
-9,K,0			0 71 -76			-8 71 71			6 10* 0			-10,K,-3			-1 116 -119			-2 32 32			-2 78 -80									-2 42 -38			-1 17 16		
			1 103 -101			-7 15 8									0 153 155			-1 155 -160			-1 15 9			-11,K,-2			-11,K,2			-1 12 -7			0 22 -21		
-8 73 72			2 178 -179			-6 28 -24			-9,K,8						1 54 55			0 37 39			0 13 -9									0 42 -45			1 29 -26		
-7 145 -142			3 131 -129			-5 114 -110						-4 37 -33			2 109 109			1 126 -125			1 55 50			-3 38 33			-5 41 34			1 118 -112					
-6 34 -35			4 22 -18			-4 32 31			-6 40 -41			-2 134 -139			3 88 90			2 14 -12			2 61 56			-2 36 -38			-4 22 -23			2 158 155					

Columns are k, $10F_o$, $10F_c$. F_o and F_c are on an absolute scale. These values do not include corrections for extinction or anomalous dispersion. Unobserved reflections are those less than $2\sigma(I)$ and are marked by*.

Table 3 Hydrogen positions in $CaHPO_4$

	electron density difference synthesis			least squares refinements			calculated		
	x	y	z	x	y	z	x	y	z
H(1)	.43	.29	.96	.44	.27	.95	.454	.267	.933
H(2)	.0	.0	.0	.0	.0	.0	.016	.015	.031
H(3)	.54	.14	.43	.56	.17	.48	.516	.081	.444

The calculated hydrogen positions were used to obtain distances mentioned in the tables and the text.

Table 4

Interatomic distances and angles in $CaHPO_4$

Atoms	Distance, Å, or angle, deg.
P(1), O(1)	1.5925(9) Å
P(1), O(2)	1.5397(8)
P(1), O(3)	1.5177(9)
P(1), O(4)	1.5147(9)
O(1), P(1), O(2)	108.10(5)°
O(1), P(1), O(3)	109.40(5)
O(1), P(1), O(4)	106.59(5)
O(2), P(1), O(3)	111.23(5)
O(2), P(1), O(4)	107.45(5)
O(3), P(1), O(4)	113.81(5)
O(1), O(2)	2.536(1) Å
O(1), O(3)	2.539(1)
O(1), O(4)	2.492(1)
O(2), O(3)	2.523(1)
O(2), O(4)	2.463(1)
O(3), O(4)	2.540(1)
P(2), O(5)	1.5244(9)
P(2), O(6)	1.5459(10)
P(2), O(7)	1.5482(9)
P(2), O(8)	1.5125(10)
O(5), P(2), O(6)	110.43(6)°
O(5), P(2), O(7)	109.59(5)
O(5), P(2), O(8)	110.64(6)
O(6), P(2), O(7)	104.78(6)
O(6), P(2), O(8)	110.58(7)
O(7), P(2), O(8)	110.70(6)
O(5), O(6)	2.522(1) Å
O(5), O(7)	2.511(1)
O(5), O(8)	2.497(1)
O(6), O(7)	2.451(1)
O(6), O(8)	2.514(1)
O(7), O(8)	2.518(1)
environments	
O(1), H(1)	1.00 }
O(6), H(3)	1.00 } assumed
O(7), H(2)	1.00 }

Table 4
(cont'd)

O(1), Ca(1)		2.4142(9)
O(1), O(5)		2.565(1)*
H(1), O(5)		1.59**
O(1), H(1), O(5)		165°
P(1), O(1), O(5)		118.52(5)
O(2), Ca(1)		2.4223(9) Å
O(2), Ca(1′)		2.4482(9)
O(2), Ca(2)		2.5718(9)
O(3), Ca(2)		2.379(1)
O(3), Ca(2′)		2.4785(9)
O(4), Ca(1)		2.2951(9)
O(4), Ca(2)		2.4796(9)
O(5), Ca(2)		2.433(1)
O(5), H(1)		1.59
O(5), O(1)		2.565(1)*
O(6), Ca(1)		2.450(1)
O(6), Ca(2)		2.518(1)
O(6), H(3)		2.24
O(6), O(8′)		2.669(1)*
H(3), O(8′)		1.87
O(6), H(3), O(8′)		140°
P(2), O(6), O(8′)		139.53(7)
O(7), Ca(6)		2.5098(9) Å
O(7), Ca(1)		2.763(1)
O(7), O(7′)		2.458(2)*
O(7), H(1)		1.46
O(7), H(1), O(7′)		178°
P(2), O(7), O(7′)		108.29(6) Å
O(8), Ca(1)		2.363(1)
O(8), Ca(2)		2.483(1)
O(8), O(6′)		2.669(1)*
O(8), H(3′)		1.87

* Hydrogen bond between these two oxygens.
** Distances and angles involving hydrogen were obtained using the calculated hydrogen positions.

The figures in parentheses are standard deviations in the last digit of the interatomic distances and angles, and were calculated from the standard deviation in the atomic positional parameters and the unit cell parameters. They include terms from the variance-covariance matrix.

Figure Legends

1. A stereo illustration of the crystal structure of $CaHPO_4$, viewed along [010]. The origin of the crystallographic coordinate system is marked by *. The $CaHPO_4$ chains are seen nearly end on.

2. The calcium ion coordinations in:

   a) $CaHPO_4$ [Ca(1)]
   b) $CaHPO_4$ [Ca(2)]
   c) $CaSO_4$
   d) $CaHPO_4 \cdot 2H_2O$
   e) $CaSO_4 \cdot 2H_2O$
   f) $Ca(H_2PO_4)_2 \cdot H_2O$

   The direction of the $Ca-XO_4$ chain runs from the top to the bottom of the drawing in each case. The similarities in the structures can be seen from the XO_4-Ca-XO_4 sequences in the centers of the drawings and from the two XO_4 groups to the left of each of these sequences (in Fig. 2f, these two XO_4 groups are shown behind rather than to the left of the chain sequence). The latter XO_4 groups define the positions of the two chains in the corrugated sheet which are adjacent to the chain that is shown.

3. The PO_4 ion environments in $CaHPO_4$.

   a) the $P(1)O_4$ group.
   b) the $P(2)O_4$ group.

   Two sites for H(2) are very close together. Only one of these sites may be occupied at any given time. The same is true for the two adjacent H(3) sites.

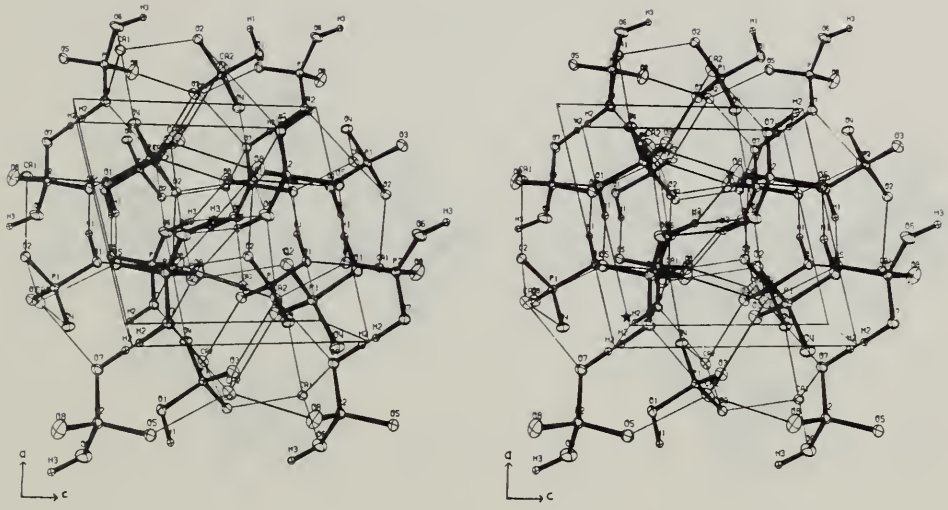


Figure 1. A stereo illustration of the crystal structure of $CaHPO_4$, viewed along [010]. The origin of the crystallographic coordinate system is marked by *. The $CaHPO_4$ chains are seen nearly end on.

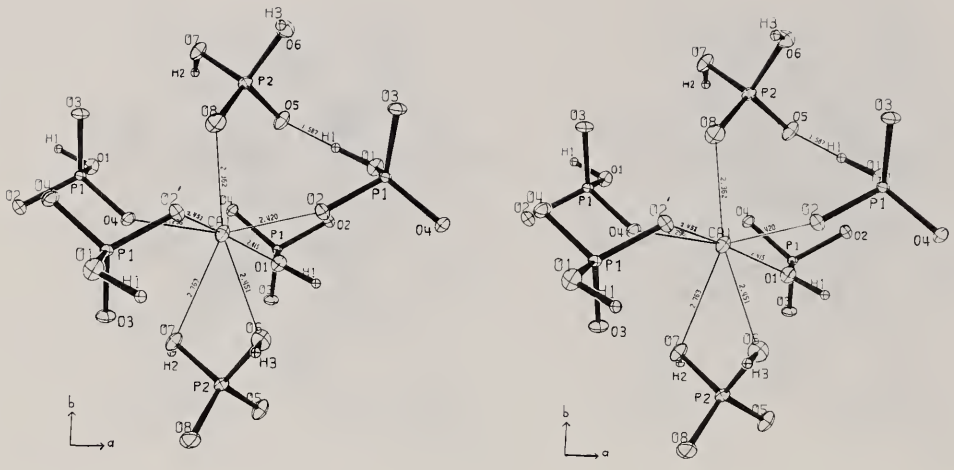


Figure 2a. The calcium ion coordination in $CaHPO_4$ [Ca(1)]. The direction of the $CaXO_4$ chain is vertical.

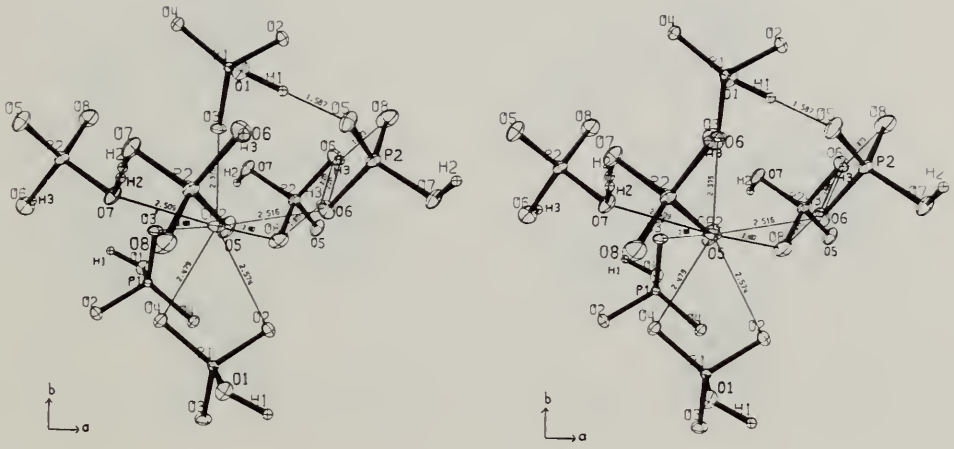


Figure 2b. The calcium ion coordination in $CaHPO_4$ [Ca(2)]. The direction of the $CaXO_4$ chain is vertical.

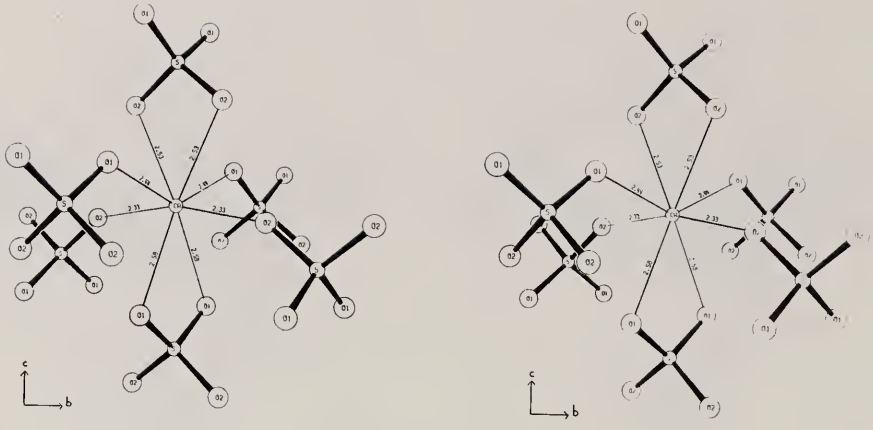


Figure 2c. The calcium ion coordination in $CaSO_4$. The direction of the $CaXO_4$ chain is vertical.

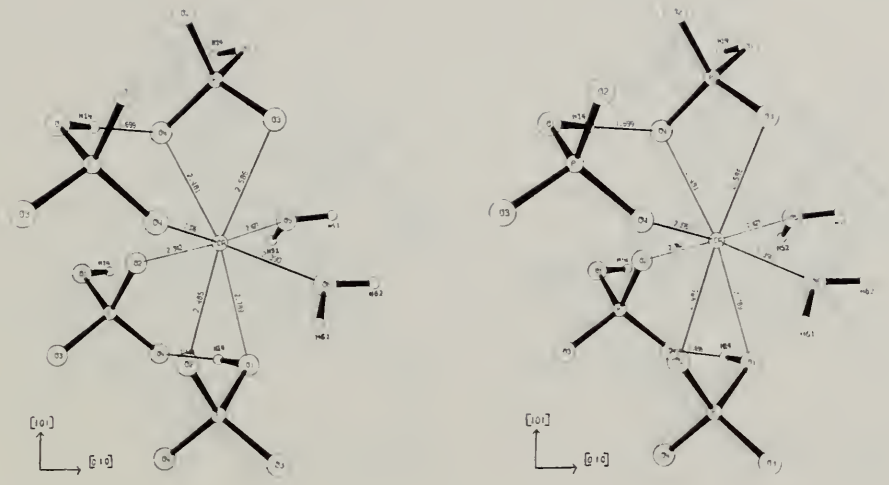


Figure 2d. The calcium ion coordination in $CaHPO_4 \cdot 2H_2O$. The direction of the $CaXO_4$ chain is vertical.

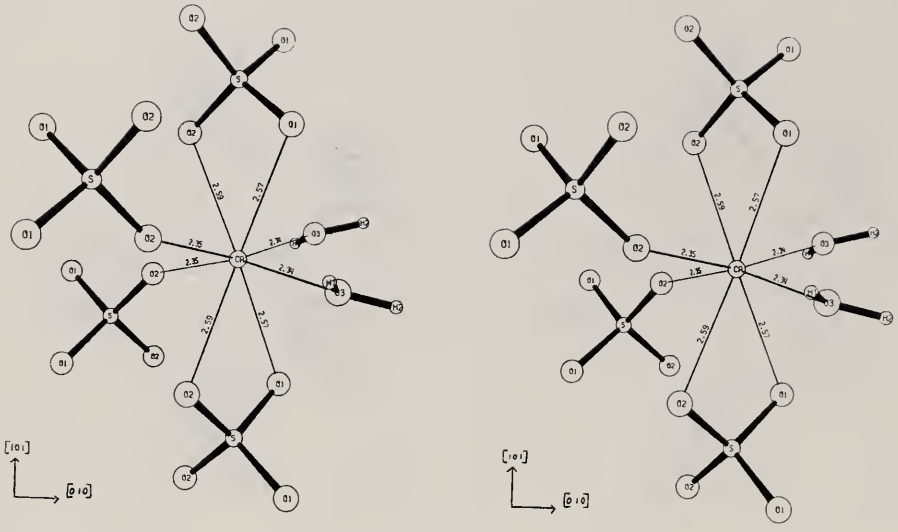


Figure 2e. The calcium ion coordination in $CaSO_4 \cdot 2H_2O$. The direction of the $CaXO_4$ chain is vertical.

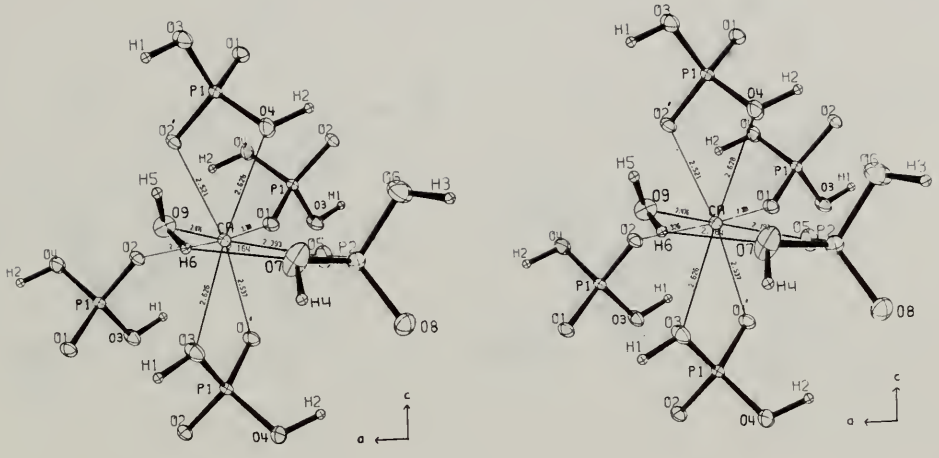


Figure 2f. The calcium ion coordination in $Ca(H_2PO_4)_2 \cdot H_2O$. The direction of the $CaXO_4$ chain is vertical.

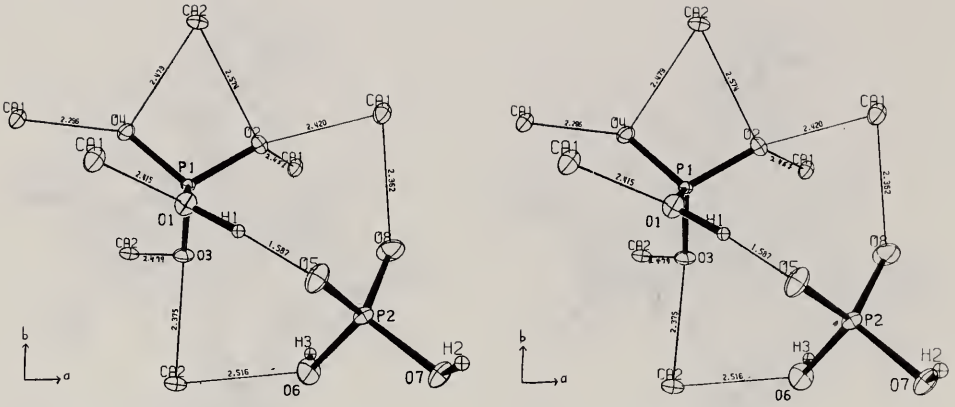


Figure 3a The PO_4 environment in $CaHPO_4$, the $P(1)O_4$ group.

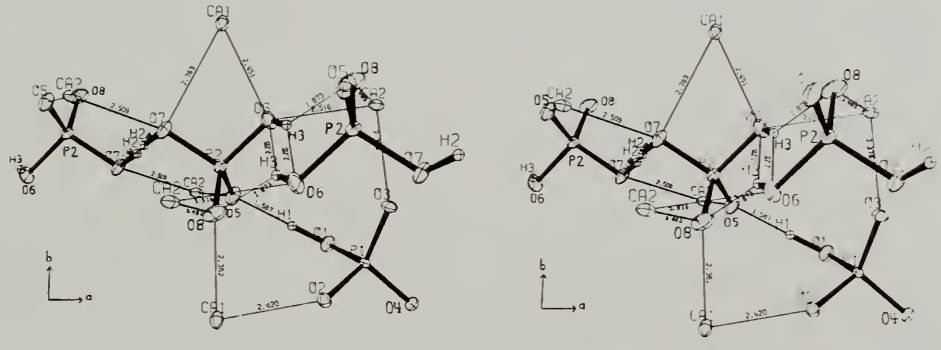


Figure 3b. The PO_4 environment in $CaHPO_4$, the $P(2)O_4$ group.