

as  $\text{H}_3\text{O}^+$  (or  $\text{NH}_4^+$ ) rather than as a single  $\text{H}^+$  (Kreuer, Rabenau & Weppner, 1982). It is, however, not easy to envisage by this mechanism why such a marked reduction in conductivity should occur for the ammonium-substituted compound. The number of potential hydrogen carriers (whether  $\text{H}_3\text{O}^+$  or  $\text{NH}_4^+$ ) is the same in both systems. On the other hand, the number of hydrogen vacancies in  $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$  is drastically reduced by the filling of the in-square hydrogen bonds, suggesting that a mechanism involving proton jumps between filled and unfilled sites is dominant.

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## A Glaserite-Type Structure: Calcium Tripotassium Hydrogenbis(phosphate), $\text{CaK}_3\text{H}(\text{PO}_4)_2$

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**Abstract.**  $M_r = 348.34$ , monoclinic, space group  $C2/m$ ,  $a = 9.878$  (1),  $b = 5.735$  (1),  $c = 7.436$  (1) Å,  $\beta = 94.28$  (1)°,  $V = 420.08$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 2.77$ ,  $D_x = 2.754$  Mg m<sup>-3</sup> at 298 K,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 2.65$  mm<sup>-1</sup>. Final  $R = 0.017$  for 512 observed reflections. The structure consists of columns of cations, Ca and K(1), and columns of cations and anions, K(2) and  $\text{PO}_4$ . The arrangement of these columns in a pseudo-hexagonal form is similar to that of glaserite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ , e.g.  $\alpha\text{-Ca}_3(\text{PO}_4)_2$  (Mathew, Schroeder, in a symmetric hydrogen bond across a crystallographic center of inversion to form a dimeric  $[\text{H}(\text{PO}_4)_2]$  unit.

**Introduction.** A number of calcium phosphates are known to have structures related to glaserite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ , e.g.  $\alpha\text{-Ca}_3(\text{PO}_4)_2$  (Mathew, Schroeder, Dickens & Brown, 1977),  $\text{Ca}_5(\text{SiO}_4)(\text{PO}_4)_2$  (Dickens & Brown, 1971*a*), and  $\text{Ca}_7\text{Mg}_9(\text{Ca},\text{Mg})_2(\text{PO}_4)_{12}$  (Dickens & Brown, 1971*b*). However, none of these compounds contains  $\text{HPO}_4$  groups.  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ , which contains

an acidic  $\text{PO}_4$  group, has been proposed to be related to glaserite (Brown & Fowler, 1967; Grenier, Durif & Martin, 1969; Dickens & Brown, 1972). A structural study was therefore undertaken to elucidate any relationship with other glaserite-type compounds.

**Experimental.** Crystals were prepared by the method used by Frazier, Smith, Lehr & Brown (1962). The X-ray powder pattern, refractive indices, cell parameters and space group obtained for this study agreed with the reported values (Frazier *et al.*, 1962). Precession photographs showed monoclinic symmetry  $2/m$ , although they showed marked pseudotrigonal symmetry. Systematic absences of  $hkl$  for  $h+k = 2n+1$  indicated the possible space groups  $Cm$ ,  $C2$  and  $C2/m$ . The centrosymmetric space group  $C2/m$ , initially chosen, was confirmed by the structure analysis and refinements.

Thin platy crystal  $0.02 \times 0.14 \times 0.18$  mm used for measurement of precise cell constants and three-dimensional intensity data, automatic four-circle dif-

fractometer, graphite-monochromated Mo K $\alpha$  radiation, cell parameters obtained by least-squares fit of  $2\theta$  values of 15 reflections ( $19 < 2\theta < 35^\circ$ ) measured by automatically centering at positive  $2\theta$  values; total of 1767 reflections in the hemisphere ( $hkl$ ,  $h\bar{k}l$ ,  $hkl$  and  $h\bar{k}l$ ) up to  $2\theta = 55^\circ$  measured using  $\theta - 2\theta$  scan technique and variable scan rate of  $0.5$  to  $29.3^\circ \text{ min}^{-1}$  depending on the intensity of each reflection, background counts made for half the scan time at each end of scan range; four reflections measured every 30 reflections showed no apparent change in their intensities during the data collection; e.s.d. in intensity  $\sigma(I)$  calculated from  $\sigma^2(I) = (\text{total counts}) + c(\text{total counts})^2$  where total counts is the scan counts and background counts and  $c (= 0.00027)$  is the instability factor determined from the data for four standard reflections, intensities corrected for Lorentz and polarization effects and for absorption, maximum and minimum absorption corrections to intensities 1.347 and 1.050 respectively, equivalent reflections merged into a set of 540 unique reflections, 512 with  $F_o > 3\sigma(F_o)$  considered observed and used in the structure analysis; equivalent reflections agreed within 2.1% on average (based on  $F$ ).

In the space group  $C2/m$ , all heavy atoms (Ca, K and P) must be in special positions. On this basis, the positions of these atoms were easily deduced from a three-dimensional Patterson synthesis. The positions of the remaining atoms were located in subsequent Fourier syntheses. There are only two H atoms per unit cell and these were found to be at centers of inversion.

Refinement by full-matrix least squares, quantity minimized  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/\sigma^2(F_o)$ , scattering factors used were those of Cromer & Mann (1968) for neutral Ca, K, P and O atoms and that of Stewart, Davidson & Simpson (1965) for H,  $F(000) = 344$ , dispersion corrections for Ca, K, P and O taken from *International Tables for X-ray Crystallography* (1974), all calculations performed with program XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); non-H atoms refined with anisotropic thermal parameters and the H atom with a fixed isotropic parameter ( $U = 0.017 \text{ \AA}^2$ ); an isotropic secondary extinction correction (Zachariasen, 1967) was applied and the extinction parameter refined to  $0.4 (1) \times 10^{-5} \text{ mm}^{-1}$ ; final  $R$  and  $R_w = 0.017$  and  $0.021$  respectively for observed reflections,  $0.018$  and  $0.021$  for unique reflections, goodness-of-fit = 1.77 and final average and maximum shift-to-error ratios for the atomic parameters  $0.001$  and  $0.002$  respectively.

**Discussion.** Final atomic parameters are listed in Table 1.\*

\* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38195 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{PO}_4^{3-}$  ions are packed in two types of columns along  $[001]$ , one containing only the cations Ca and K(1), and the other both cations, K(2), and anions,  $\text{PO}_4$ . Each cation column is surrounded by six cation-anion columns and in turn each cation-anion column by three cation columns and three cation-anion columns arranged alternately (Fig. 1). The arrangement of these columns in a pseudo-hexagonal form is similar to that of glaserite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$  (Gossner, 1928; Okada & Oosaka, 1980). The pseudo-hexagonal primitive cell corresponding to that of glaserite (outlined in Fig. 1) contains cation columns at the corners and cation-anion columns on the major diagonal as in glaserite (Fig. 2).

Table 1. Final atomic parameters for  $\text{CaK}_3\text{H}(\text{PO}_4)_2$

E.s.d.'s are given in parentheses.

|      | x           | y          | z           | $U_{eq}^*(\text{\AA}^2)$ |
|------|-------------|------------|-------------|--------------------------|
| Ca   | 0.0         | 0.0        | 0.0         | 0.0084 (4)               |
| K(1) | 0.0         | 0.0        | 0.5         | 0.0250 (6)               |
| K(2) | 0.33047 (5) | 0.0        | 0.80904 (7) | 0.0143 (4)               |
| P    | 0.33947 (5) | 0.0        | 0.25110 (7) | 0.0078 (4)               |
| O(1) | 0.1852 (2)  | 0.0        | 0.2172 (2)  | 0.013 (1)                |
| O(2) | 0.3759 (2)  | 0.0        | 0.4589 (2)  | 0.018 (1)                |
| O(3) | 0.4014 (1)  | 0.2186 (2) | 0.1718 (1)  | 0.016 (1)                |
| H    | 0.5         | 0.0        | 0.5         |                          |

$$* U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j \text{ (Hamilton, 1959).}$$

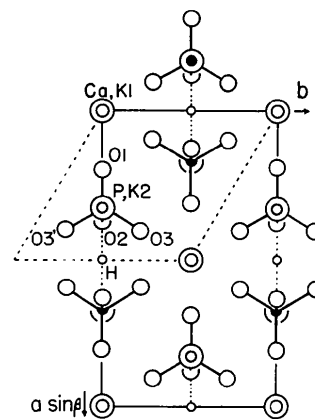


Fig. 1. Contents of the unit cell of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  projected down the  $c$  axis.

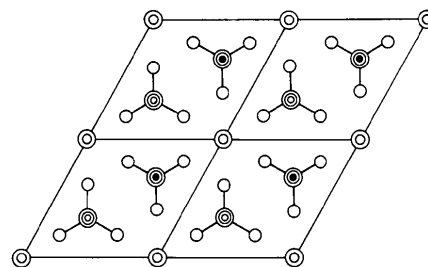


Fig. 2. A schematic drawing of the structure of glaserite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$ . One S, O, K column in the unit cell points 'up' and the other points 'down'. The Na, K columns define the cell corners.

The cation column is linear since both cations Ca and K(1) are in special positions. The cation-anion column is also nearly linear if we consider only K(2) and P atoms. In glaserite, one of the O atoms of the  $\text{SO}_4$  group is also along this column, consistent with trigonal symmetry. In  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ , the corresponding O atom, O(2), is markedly off the column of K(2) and P atoms (Fig. 1).

The environments of the cations in glaserite and  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  are quite similar. However, there is a slight reduction in the coordination numbers of the  $\text{K}^+$  ions in  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ , as expected, due to the presence of the covalently bonded H atom on one O of the  $\text{PO}_4$  group and the displacement of O(2) from the column of K(2) and P atoms. In glaserite, the  $\text{K}^+$  ions in the cation columns are coordinated to 12 O atoms from six shared edges of  $\text{SO}_4$  ions. The geometry corresponds to a trigonal antiprism with six additional meridional O atoms in a hexagonal outline. In  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  the corresponding  $\text{K}^+$  ions, K(1), have only ten  $\text{K}\cdots\text{O}$  contacts less than 3.5 Å (range 2.888–3.125 Å) consisting of four shared edges and two apexes of the  $\text{PO}_4$  ions. Although an approximate trigonal antiprism arrangement of O atoms around K(1) is retained, two meridional O atoms, O(2), are bent away from K(1) with these  $\text{K}(1)\cdots\text{O}(2)$  distances > 3.5 Å.

The environment of the  $\text{K}^+$  ions in the cation-anion columns in glaserite consists of ten O atoms, comprising one face, three shared edges and an apex of  $\text{SO}_4^{2-}$  ions. The arrangement of O atoms around K(2) in the cation-anion column in  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  is nearly identical to that in glaserite. However, one of the O atoms corresponding to the face coordination in glaserite [O(1)] is at a distance of 3.453 Å from K(2). This is significantly larger than the sum of the ionic radii (Shannon, 1976) and indicates that there is no appreciable bonding. Thus the face coordination in glaserite is reduced to an edge-sharing in  $\text{CaK}_3\text{H}(\text{PO}_4)_2$ .

As in the case of the  $\text{Na}^+$  ions in glaserite, the environment of the  $\text{Ca}^{2+}$  ions in  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  consists of six O atoms forming a distorted octahedron.

The dimensions of the  $\text{PO}_4$  group are given in Table 2. The P–O(2) bond length, 1.560 Å, supports the assignment of a covalently bonded H atom on O(2). The remaining P–O distances (mean 1.530 Å) are in good agreement with the mean value of 1.536 Å calculated for orthophosphate groups (Baur, 1974).

The two  $\text{PO}_4$  groups in the unit cell, related by a center of inversion, are linked together through an apparently 'symmetric' hydrogen bond with the H atom at the center of inversion forming an  $\text{H}(\text{PO}_4)_2$  dimer. The  $\text{O}(2)\cdots\text{O}(2')$  distance, 2.483 Å, is in the range of values, 2.40–2.55 Å, quoted for symmetric hydrogen bonds (Hamilton & Ibers, 1968). Similar linkages of  $\text{HPO}_4^{2-}$  ions are known in several phosphates (Dickens, Bowen & Brown, 1972; Takagi, Mathew & Brown, 1980, 1982).

Table 2. Selected bond lengths (Å) and angles (°) for  $\text{CaK}_3\text{H}(\text{PO}_4)_2$

| E.s.d.'s are given in parentheses. |               |                    |               |
|------------------------------------|---------------|--------------------|---------------|
| P–O(1)                             | 1.526 (2)     | O(1)–P–O(2)        | 108.5 (1)     |
| P–O(2)                             | 1.560 (2)     | O(1)–P–O(3)        | 111.0 (1) × 2 |
| P–O(3)                             | 1.532 (1) × 2 | O(2)–P–O(3)        | 108.2 (1) × 2 |
|                                    |               | O(3)–P–O(3)        | 109.8 (1)     |
| Ca $\cdots$ O(1)                   | 2.348 (1) × 2 | K(2) $\cdots$ O(1) | 3.453 (1)     |
| Ca $\cdots$ O(3)                   | 2.318 (1) × 4 | K(2) $\cdots$ O(1) | 2.878 (1) × 2 |
|                                    |               | K(2) $\cdots$ O(2) | 2.675 (2)     |
| K(1) $\cdots$ O(1)                 | 2.888 (2) × 2 | K(2) $\cdots$ O(3) | 2.814 (1) × 2 |
| K(1) $\cdots$ O(2)                 | 3.125 (2) × 4 | K(2) $\cdots$ O(3) | 2.924 (1) × 2 |
| K(1) $\cdots$ O(3)                 | 3.026 (2) × 4 | K(2) $\cdots$ O(3) | 3.010 (1) × 2 |

Glaserite-type structures have been observed or can be predicted for compounds of the type  $(A, C)_2\text{BX}_4$  where A and C are cations differing in size and  $\text{BX}_4$  is a tetrahedral anion. However, a large number of compounds of the type  $\text{A}_2\text{BX}_4$  have been shown to be related to the glaserite structure (Eysel, 1973; Moore, 1973).

Calcium phosphates known to possess geometries related to glaserite are  $\alpha\text{-Ca}_3(\text{PO}_4)_2$  (Mathew *et al.*, 1977),  $\text{Ca}_7\text{Mg}_9(\text{Ca, Mg})_2(\text{PO}_4)_{12}$  (Dickens & Brown, 1971*b*) and silicocarnotite,  $\text{Ca}_5(\text{SiO}_4)(\text{PO}_4)_2$  (Dickens & Brown, 1971*a*). None of these compounds has a 2:1 ratio of cations and anions as in glaserite, with the result that their emulation of the glaserite-type structure requires cation vacancies. Although the detailed environments of the cations in these compounds are different from those of the cations in glaserite, as expected from the size of the ions and the vacancies, a pseudohexagonal arrangement of the columns of cations and cation-anions is evident.  $\text{CaKPO}_4$  may be a typical example of the glaserite-type structure but a detailed structure analysis has not been performed.

To our knowledge,  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  is the first example of a compound structurally related to glaserite which contains an acidic phosphate group. Since the radius ratio of the cations in  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  is nearly identical to that of glaserite and the 2:1 ratio of cations and anions is maintained, the presence of the proton on the  $\text{PO}_4$  group causes only very minor structural changes.

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