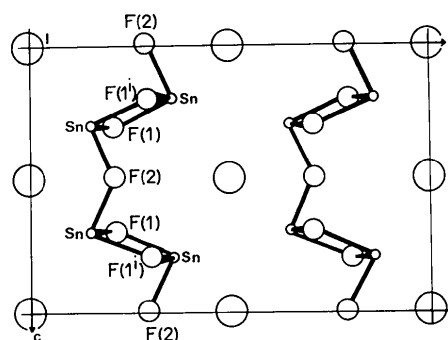
Fig. 1. Couche $(\text{Sn}_2\text{F}_3)_n^+$ parallèle au plan yOz .

sommet, ce qui donne naissance à des couches parallèles au plan yOz aux cotes $x \approx 0,25$ et $x \approx 0,75$ (Fig. 1). Ainsi, deux types de fluor existent dans ces couches: F(1) triplement lié et F(2) ponté. Les liaisons Sn-F sont anormalement longues (Tableau 2) sauf la liaison du fluor ponté qui a la valeur normale observée pour ce type de liaison [Sn-F(2) = 2,195 Å].

Les ions I^- se disposent entre ces feuillettes (Fig. 2) à des cotes voisines de $x = 0$ et $x = 0,5$. Ils ne forment que des liaisons faibles de type interactions de van der Waals: Sn-I varie de 3,53 à 3,92 Å. Chaque atome d'iode est environné par huit atomes d'étain placés aux sommets d'un cube très déformé (Tableau 2).

Si on tient compte de tous les atomes placés à des distances inférieures à la somme des rayons de van der Waals, le polyèdre de coordination autour de Sn^{II} est un antiprisme à base carrée monocapé déformé SnF_4I_4E . On suppose alors que la paire libre E est orientée vers la base carrée formée par les quatre atomes d'iode.

Dans Sn_2IF_3 , on observe donc une structure en

Fig. 2. Projection de la structure sur le plan xOz .

couches. Les anions I^- viennent se disposer entre les couches cationiques $(\text{Sn}_2\text{F}_3)_n^+$. L'arrangement des atomes de fluor autour de l'étain est analogue à celui observé dans SnClF (Geneys, Vilminot & Cot, 1976), mais les doubles chaînes formées sont reliées entre elles pour former des couches alors qu'elles sont isolées dans SnClF . On constate aussi que l'atome d'iode n'est pas lié à l'étain, résultat analogue à celui observé pour le chlore dans Sn_2ClF_3 (Donaldson, Laughlin & Puxley, 1977), et pour le brome dans Sn_3BrF_5 (Vilminot, Granier & Cot, 1978).

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Triclinic Barium Dihydrogenphosphate

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Abstract. $\text{Ba}(\text{H}_2\text{PO}_4)_2$, $P\bar{1}$, $a = 7.0334$ (11), $b = 109.46$ (1), $\gamma = 96.02$ (2) $^\circ$ at 295 K ($\lambda = 0.70926$ Å), 8.0437 (15), $c = 7.2158$ (7) Å, $\alpha = 104.45$ (1), $\beta = Z = 2$, $D_x = 3.03$, $D_m = 2.99$ g cm $^{-3}$. An open two-

dimensional network of PO_4 groups is formed by hydrogen-bonded dimers linked together by short hydrogen bonds [2.452 (4) and 2.490 (3) Å] across inversion centers. The PO_4 nets are linked by Ba—O coordination bonds. The nine Ba—O distances range from 2.676 to 2.967 Å. The average P—O distances are: P—OH 1.580, P—OH (H on $\bar{1}$) 1.528 and P—O 1.501 Å.

Introduction. Colorless rhombic platelets of triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ were grown from a solution of 5 g of barium phosphate in 55 g of a 17.9% aqueous solution of H_3PO_4 by evaporation at 55°C. A triclinic space group is indicated by $\bar{1}$ Laue symmetry and the refinement process* confirmed our selection of $P\bar{1}$. Crystal density was measured by flotation in a mixture of tetrabromoethane and diiodomethane.

The data crystal was cut to approximately $0.3 \times 0.5 \times 1.2$ mm and mounted on a four-circle automated diffractometer with ϕ approximately along $[\bar{1}\bar{1}, \bar{3}, 10]$, the longest dimension. Cell constants were determined by a least-squares fit to 2θ , ω and χ values measured with the resolved $\text{Mo } K\alpha_1$ line for 30 reflections in the range $84 < 2\theta < 88^\circ$. Intensity data for 13 381 reflections (the full sphere) were measured out to $2\theta = 90^\circ$ by $\theta-2\theta$ step scans (step interval 0.03° in 2θ , 1 s count per step, 10 s each background, $\text{Mo } K\alpha$ radiation, 0.001 in Nb filter, Y—Zr balanced filters with $2\theta < 12^\circ$). As provided in the diffractometer control program (Lenhart, 1975), coincidence losses were corrected and reflections were rescanned once if $I/\sigma(I)$ was less than 10. The three monitor reflections showed an intensity decrease of 1% in 650 h of X-ray exposure.

Absorption corrections were calculated by the computer program *ORABS* (Wehe, Busing & Levy, 1962) using a linear absorption coefficient of 58.89 cm^{-1} and a $9 \times 9 \times 9$ Gaussian grid. The maximum, minimum and average transmission factors were 0.2520, 0.0742 and 0.1711. Symmetry-related reflections were averaged to give 5998 F_o values including two with $F_o < 0$. Further details of the data-collection and data-reduction procedures have been given previously (Miller, Lenhart & Joesten, 1972).

A sharpened Patterson map yielded coordinates for all Ba and P, and most O atoms. Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$; σ was calculated from the counting statistics and included an experimentally determined instability factor (0.85%). All atoms except H were refined anisotropically along with an isotropic extinction parameter [$r^* = 3.16(4) \times 10^{-5}$ cm; Zachariasen, 1968]. All H atoms were located from a difference synthesis. Three were near O atoms with typically long P—O distances and O—O distances characteristic

* An attempt to refine in space group $P\bar{1}$ gave very large correlations between the parameters of atoms related by inversion in $P\bar{1}$.

Table 1. *Positional parameters for triclinic* $\text{Ba}(\text{H}_2\text{PO}_4)_2$,

	x	y	z
Ba	0.26661 (1)	0.09225 (1)	0.29432 (1)
P(1)	0.76038 (6)	0.09677 (5)	0.27535 (6)
P(2)	0.29004 (7)	0.57713 (5)	0.19878 (6)
O(1)	0.63827 (20)	-0.01592 (17)	0.34970 (20)
O(2)	0.84399 (20)	0.01569 (20)	0.11656 (19)
O(3)	0.61360 (24)	0.22134 (23)	0.20139 (27)
O(4)	0.96002 (21)	0.21510 (22)	0.46299 (21)
O(5)	0.15044 (20)	0.70731 (16)	0.20669 (19)
O(6)	0.46809 (21)	0.60993 (18)	0.40456 (21)
O(7)	0.36469 (24)	0.57773 (20)	0.02320 (23)
O(8)	0.16765 (22)	0.38567 (17)	0.15228 (21)
H(1)	0.6505 (57)	0.2917 (49)	0.1492 (57)
H(2)	0.9525 (49)	0.2315 (43)	0.5911 (52)
H(3 $\bar{6}$)	0.5	0.5	0.5
H(37)	0.5	0.5	0.0
H(4)	0.1058 (53)	0.3497 (46)	0.0718 (53)

of hydrogen bonding (Table 2). The remaining H atoms were located on two inversion centers between O(6)—O(6') and O(7)—O(7'). The free coordinates of the H atoms were refined.

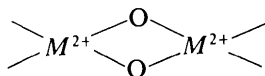
Atomic scattering factors for Ba^{2+} , P, and O atoms were those tabulated by Cromer & Mann (1968); the curve for H was that of Stewart, Davidson & Simpson (1965). Anomalous-dispersion factors (Cromer & Liberman, 1970) were used for Ba^{2+} and P. Except as otherwise noted, calculations were with the XRAY 67 program system (Stewart, 1967), as modified and updated for the Vanderbilt University Sigma 7 computer.

The final refinement cycle, including all reflections, gave a conventional R of 0.022, a weighted residual $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$ of 0.038, a standard error of an observation of unit weight of 5.98 and a maximum shift-to-error ratio of 0.19. The final difference map showed maximum and minimum $\Delta\rho$ values of $\pm 1.5 \text{ e } \text{Å}^{-3}$, both near the Ba^{2+} position. The final positional parameters are reported in Table 1.*

Discussion. The orthorhombic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ structure has been reported previously (Gilbert, Lenhart & Wilson, 1977; Prelesnik, Herak, Čurić & Krstanović, 1978). The cell constants, space group and density of triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ have been reported by Lehr, Brown, Frazier, Smith & Thrasher (1967) and a note on the structure was published by Herak & Krstanović (1975). Our study of $\text{Ba}(\text{H}_2\text{PO}_4)_2$ is part of a program of research on the magnetic properties of phosphate crystals. The crystal structure of triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ is illustrated in Figs. 1 and 2 and selected interatomic distances and angles are displayed in Table 2.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33666 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal packing in triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ differs substantially from that of the calcium phosphate analog $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (Dickens, Prince, Schroeder & Brown, 1973), the calcium arsenate analog $\text{Ca}(\text{H}_2\text{AsO}_4)_2$ (Ferraris, Jones & Yerkess, 1972) and the orthorhombic form of $\text{Ba}(\text{H}_2\text{PO}_4)_2$. An infinite



chain is found in triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ and similar chains occur in the other phosphate structures. The metal coordination is eightfold in $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and orthorhombic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ but ninefold in triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$. The nine O atoms lie within 3 Å of Ba^{2+} at an average distance of 2.815 Å; the next nearest O is 3.86 Å away. The coordination sphere includes two PO_4 edges, both from $\text{P}(1)\text{O}_4$.

The hydrogen-bond network is two-dimensional in both $\text{Ba}(\text{H}_2\text{PO}_4)_2$ structures, three-dimensional in $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and $\text{Ca}(\text{H}_2\text{AsO}_4)_2$. As shown in Figs. 1 and 2, the $\text{P}(2)\text{O}_4$ groups of triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ are linked into dimers by a pair of $\text{O}(8)-\text{H}(4)\cdots\text{O}(5')$ bonds across the center at $0, \frac{1}{2}, 0$. These dimers are linked into a two-dimensional net parallel to (010) by a series of short hydrogen bonds, $\text{O}(6)\cdots\text{O}(6')$ and $\text{O}(7)\cdots\text{O}(7')$, across the centers at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$.* This arrangement leaves an open pocket with no atom closer than 2.2 Å to the center at $0, \frac{1}{2}, \frac{1}{2}$ and only two, O(4) and H(2), within 3 Å. The $\text{P}(1)\text{O}_4$ groups are attached to the 'top' and 'bottom' of the $\text{P}(2)\text{O}_4$ sheet by the $\text{O}(3)-\text{H}(1)\cdots\text{O}(7)$ and $\text{O}(4)-\text{H}(2)\cdots\text{O}(5)$ hydrogen bonds. The phosphate sheets are held together by Ba^{2+} which makes six of its nine coordination bonds with $\text{P}(1)\text{O}_4$ O atoms. No hydrogen bonds cross the region between the $\text{P}(1)\text{O}_4$ - $\text{P}(2)\text{O}_4$ sheets described above.

This arrangement differs from the $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and

* These O—O distances, 2.490 and 2.452 Å, fall in the region of symmetrical hydrogen bonds on the Nakamoto–Margoshes–Rundle curve (Speakman, 1972; Pimentel & McClellan, 1971). We have assumed the bonds to be symmetrical and placed the H atom on the center.

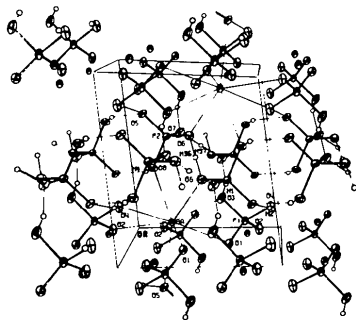


Fig. 1. Stereoview (ORTEP, Johnson, 1965) of triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ with the unit cell shown. The origin is indicated by OR; *a* is horizontal and *b* vertical. Thermal ellipsoids are at the 40% probability level.

$\text{Ca}(\text{H}_2\text{AsO}_4)_2$ structures where one phosphate group participates in a hydrogen-bonded dimer arrangement and the other forms a chain *via* symmetrical hydrogen bonds. The more compact orthorhombic $\text{Ba}(\text{H}_2\text{PO}_4)_2$ structure ($D_x = 3.21 \text{ g cm}^{-3}$) is based on a simpler two-dimensional H_2PO_4 net which lacks both the top-bottom $\text{P}(1)\text{O}_4$ groups and the open pocket of triclinic $\text{Ba}(\text{H}_2\text{PO}_4)_2$.

The P—O bonds (Table 2) in $\text{P}(1)\text{O}_4$ are normal with bonds averaging 1.580 Å for P—OH and 1.496 Å for P—O. $\text{P}(2)\text{O}_4$ is atypical with one P—OH distance of 1.580 Å, two P—OH distances, those involving the short O—O contacts, of about 1.528 Å and a P—O distance of 1.512 Å. The O—P—O angles for the shared edges in the $\text{P}(1)\text{O}_4$ tetrahedron are small, as expected (103.3°). The distortion indices (Baur, 1970, 1974) were calculated for both phosphate groups. The values* of the indices for $\text{P}(1)\text{O}_4$ are characteristic of H_2PO_4^- groups with asymmetrical hydrogen bonds and O—O edges shared with divalent cation coordination polyhedra. The indices for the less distorted $\text{P}(2)\text{O}_4$ are

* Values ($\times 10^3$) for $\text{P}(1)\text{O}_4$: DI(PO) = 27, DI(OO) = 25, DI(OPO) = 42. For $\text{P}(2)\text{O}_4$: DI(PO) = 14, DI(OO) = 21, DI(OPO) = 23.

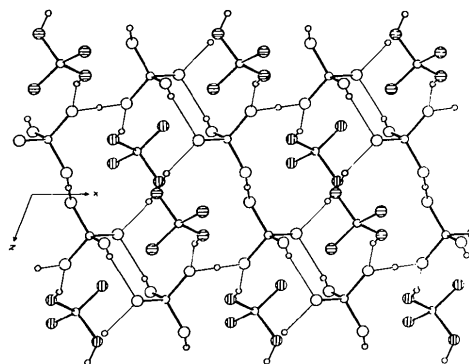


Fig. 2. The H_2PO_4 hydrogen-bonded layer projected onto the *xz* plane. The $\text{P}(2)\text{O}_4$ layer of linked dimers (see text) is shown with open circles. The $\text{P}(1)\text{O}_4$ groups above and below the dimer sheet are horizontally and vertically cross-hatched respectively.

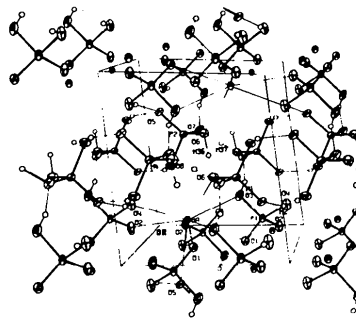


Table 2. *Interatomic distances (Å) and angles (°) for triclinic Ba(H₂PO₄)₂*

A prime indicates inversion through $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. Translations: (I) $-a$; (II) $-b$; (III) $-c$; (IV) $-a-c$; (V) $-b-c$.

Ba—O(1)	2.776 (1)	Ba—O(4) ^I	2.950 (2)
Ba—O(1') ^{II}	2.676 (2)	Ba—O(5) ^{II}	2.967 (1)
Ba—O(2) ^I	2.746 (1)	Ba—O(6') ^I	2.776 (1)
Ba—O(2') ^V	2.682 (1)	Ba—O(8)	2.861 (2)
Ba—O(3)	2.897 (2)		
P(1)—O(1)	1.495 (2)	O(1)—P(1)—O(2)	120.54 (8)
P(1)—O(2)	1.497 (2)	O(1)—P(1)—O(3)	103.27 (10)
P(1)—O(3)	1.572 (2)	O(1)—P(1)—O(4)	109.87 (8)
P(1)—O(4)	1.588 (1)	O(2)—P(1)—O(3)	111.71 (10)
		O(2)—P(1)—O(4)	103.31 (8)
		O(3)—P(1)—O(4)	107.72 (9)
O(3)—O(7') ^{III}	2.586 (3)		
O(4)—O(5')	2.697 (2)		
O(3)—H(1)	0.82 (5)	O(3)—H(1)—O(7') ^{III}	159 (3)
H(1)—O(7') ^{III}	1.80 (5)	O(4)—H(2)—O(5')	158 (3)
O(4)—H(2)	0.92 (4)	P(1)—O(3)—H(1)	119 (3)
H(2)—O(5')	1.82 (4)	P(1)—O(4)—H(2)	115 (2)
P(2)—O(5)	1.512 (2)	O(5)—P(2)—O(6)	113.13 (8)
P(2)—O(6)	1.530 (1)	O(5)—P(2)—O(7)	108.53 (9)
P(2)—O(7)	1.526 (2)	O(5)—P(2)—O(8)	110.45 (8)
P(2)—O(8)	1.580 (1)	O(6)—P(2)—O(7)	112.39 (9)
		O(6)—P(2)—O(8)	104.31 (8)
		O(7)—P(2)—O(8)	107.87 (8)
O(6)—O(6')	2.490 (3)		
O(7)—O(7') ^{III}	2.452 (4)		
O(8)—O(5') ^{IV}	2.664 (2)	O(8)—H(4)—O(5') ^{IV}	162 (5)
O(6)—H(36)	1.245	P(2)—O(6)—H(36)	124.01
O(7)—H(37)	1.226	P(2)—O(7)—H(37)	121.46
O(8)—H(4)	0.58 (3)	P(2)—O(8)—H(4)	120 (4)
H(4)—O(5') ^{IV}	2.11 (3)		

characteristic of H₂PO₄⁻ groups with symmetrical hydrogen bonds and no shared edges.

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Structure Cristalline du Phosphore de Cobalt–Molybdène: CoMoP

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(Reçu le 3 mars 1978, accepté le 8 juin 1978)

Abstract. CoMoP, orthorhombic, *Pnma*, $a = 5.827$ (3), $b = 3.711$ (2), $c = 6.780$ (4) Å, $Z = 4$, $D_m = 8.29$, D_x

$= 8.41$ g cm⁻³. Final R value is 0.044. This structure is of the ordered Co₂P-type ($C23$) with tetrahedral and