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Orthorhombic Barium Dihydrogenphosphate

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(*Received* 8 *March* 1977; *accepted* 5 *June* 1977)

Abstract. $Ba(H_2PO_4)_2$, space group *Pccn*, a = 7·7962 (10), b = 10·2574 (10), c = 8·5653 (11) Å at 295 K (λ = 1·54051 Å), Z = 4, D_x = 3·212, D_m = 3·21 g cm^{-3}. A corrugated network of hydrogen-bonded phosphate groups lies parallel to the *ac* plane with Ba—O coordination bonds running between the phosphate layers. The eight Ba—O distances range from 2·659 (2) to 2·903 (2) Å. The phosphate distances are: P—OH 1·579 (2) and 1·576 (2) Å, and P—O 1·495 (2) and 1·490 (2) Å.

Introduction. Colorless rhombic platelets of $Ba(H_2PO_4)_2$ were grown by slow evaporation from a solution of 10 g of barium phosphate in 200 g of a 10% aqueous solution of H_3PO_4. The space group, *Pccn*, is indicated by *mmm* Laue symmetry with systematic absences for $0kl$ and $h0l$ (l odd) and $hk0$ ($h + k$ odd). Crystal density was measured by flotation in a mixture of tetrabromoethane and diiodomethane.

The data crystal was cut to 0·5 × 0·45 × 0·45 mm and mounted on a four-circle automated diffractometer with φ approximately along [320]. Cell constants were determined by least-squares fit from 2θ, ω and χ values measured with the resolved Cu $K\alpha_1$ line for 25 reflections in the range $73° < 2\theta < 88°$. Intensity data for 5792 reflections were measured out to $2\theta = 90°$ by θ–2θ step scans (step interval 2θ = 0·05°) using a 0·001 in Nb filter with Mo $K\alpha$ radiation (hkl and $\bar{h}\bar{k}\bar{l}$ octants were measured). Reflections with $2\theta < 16°$ were measured with Y—Zr balanced filters (here $\pm h \pm k \pm l$ were measured). Counts were made for 2 s at each step with 10 s background counts at the end of each scan. As provided in the diffractometer control program (Lenhert, 1975), a dead-time correction was applied to each step and each scan was repeated once with background counting time increased to 20 s if $I/\sigma(I)$ was less than 10. Total X-ray exposure (50 kV, 10 mA, tube focal spot 15 × 0·75 mm) was 350 h, during which time three standard reflections showed an intensity decrease of 1%.

Symmetry-related reflections were averaged to give 2846 F_o values (82 with $F_o < 0$, which were set to zero). Absorption corrections were calculated by the computer program *ORABS* (Wehe, Busing & Levy, 1962) using a linear absorption coefficient of 6·258 cm^{-1} and an 8 × 8 × 8 Gaussian grid. The maximum, minimum and average transmission factors were 0·210, 0·091 and 0·164. Further details of the data-collection and data-reduction procedures have been published previously (Miller, Lenhert & Joesten, 1972).

Table 1. *Positional parameters for* $Ba(H_2PO_4)_2$

	x	y	z
Ba	0·75000	0·25000	0·40513 (2)
P	0·07185 (6)	0·07555 (5)	0·21029 (6)
O(1)	0·23526 (20)	0·07109 (22)	0·11901 (21)
O(2)	0·03217 (21)	−0·07210 (15)	0·24775 (23)
O(3)	−0·08076 (21)	0·14117 (16)	0·14106 (18)
O(4)	0·09408 (24)	0·14513 (18)	0·37307 (20)
H(1)	−0·05685	−0·07685	0·33333
H(2)	0·1778 (56)	0·1245 (39)	0·4272 (47)

A sharpened Patterson function yielded coordinates for all Ba, P and O atoms. The structure was refined by full-matrix least squares where $\Sigma w(|F_o| - |F_c|)^2$ was minimized. The weights were taken as $1/\sigma(F)$, where 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, $r^* = 0{\cdot}498\,(5) \times 10^{-4}$ cm (Zachariasen, 1968). H atoms were located initially from a difference electron density map. Isotropic refinement converged for H(2); the unrefined coordinates were used for H(1).

The final refinement cycle included unobserved reflections and gave a maximum shift-to-error ratio of 0·06, a conventional R of 0·033, a weighted residual R_w $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ of 0·038, and 4·95 for the standard error of an observation of unit weight. The final difference map showed a maximum $\Delta\rho$ of 2·5 e Å^{-3} and a minimum $\Delta\rho$ of −1·8 e Å^{-3}, both near the Ba position. The final positional parameters are reported in Table 1.†

Atomic scattering factors for neutral Ba, 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 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.

Discussion. The cell constants and space group for both orthorhombic and triclinic $Ba(H_2PO_4)_2$ have been reported by Lehr, Brown, Frazier, Smith & Thrasher (1967). Recently, Agre, Krol', Trunov & Serebrennikova (1976) have reported a single-crystal structure analysis for the orthorhombic crystals based on limited photographic data, but the crystal structure of the triclinic form is not known. Our interest in barium

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $Ba(H_2PO_4)_2$

P–O(1)	1·495 (2)	Ba–O(2)″	2·816 (2)
P–O(2)	1·579 (2)	Ba–O(3)′	2·659 (2)
P–O(3)	1·490 (2)	Ba–O(3)	2·847 (2)
P–O(4)	1·576 (2)	Ba–O(4)	2·903 (2)
O(1)–O(2)	2·425 (3)	O(1)–P–O(2)	104·12 (11)
O(1)–O(3)	2·573 (2)	O(1)–P–O(3)	119·08 (10)
O(1)–O(4)	2·554 (3)	O(1)–P–O(4)	112·50 (11)
O(2)–O(3)	2·529 (2)	O(2)–P–O(3)	110·96 (9)
O(2)–O(4)	2·520 (2)	O(2)–P–O(4)	106·03 (9)
O(3)–O(4)	2·410 (2)	O(3)–P–O(4)	103·61 (9)
O(2)–H(1)	1·011	P–O(2)–H(1)	109·
O(4)–H(2)	0·83 (4)	P–O(4)–H(2)	118· (3)
H(1)–O(1)′	1·672	O(2)–H(1)–O(1)′	147·
H(2)–O(1)″	1·86 (4)	O(4)–H(2)–O(1)″	149· (4)
O(2)–O(1)′	2·581 (2)		
O(4)–O(1)″	2·604 (3)		

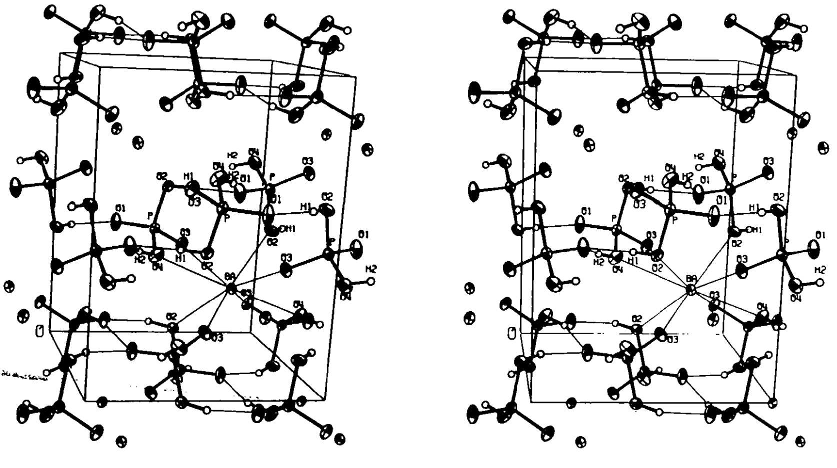

Fig. 1. Stereoview of the $Ba(H_2PO_4)_2$ crystal structure with the unit cell shown. The x axis is horizontal, the y axis is vertical and the origin is indicated by O. Thermal ellipsoids are at the 50% probability level (Johnson, 1965).

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† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32784 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

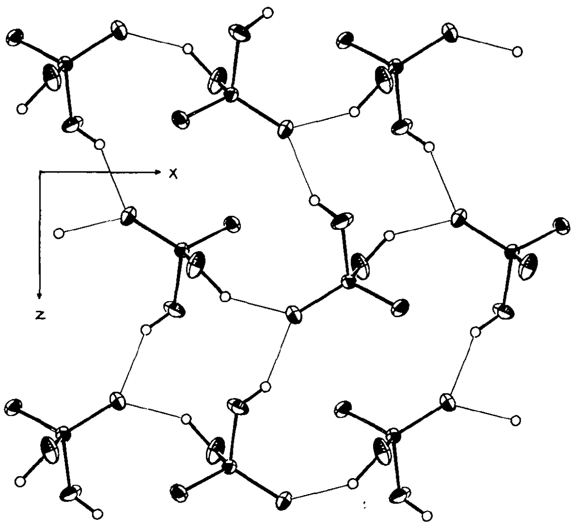

Fig. 2. The H_2PO_4 hydrogen-bonded layer viewed down the *y* axis. The middle layer of Fig. 1 is shown.

phosphate crystal structures stems from research into the magnetic properties of phosphate glasses.

Our results for the barium phosphate packing, given in Figs. 1 and 2, are in agreement with Agre *et al.* (1976). The positions of the H atoms found in the present work clarify the hydrogen bonding in the phosphate network (Fig. 2) but otherwise confirm the features discussed in the earlier paper. The $Ba(H_2PO_4)_2$ structure can be compared with two calcium phosphate structures: $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971) and $Ca(H_2PO_4)_2$ (Dickens, Prince, Schroeder & Brown, 1973). In both calcium phosphate structures the $H_2PO_4^-$ hydrogen-bonded network is three dimensional; however, the $H_2PO_4^-$ groups in $Ba(H_2PO_4)_2$ form a two-dimensional hydrogen-bonded network where the only links between layers are through the Ba—O coordination bonds. These latter bonds (see Fig. 1) tend to stabilize the 'corrugations' in the $H_2PO_4^-$ sheets.

The interatomic distances and angles displayed in Table 2 show substantially greater precision than the earlier results of Agre *et al.* (1976). The maximum Ba—O coordination distance is 2·903 (2) Å. The next nearest O atom lies 3·302 (3) Å from Ba^{2+}. As expected, the hydrogen bonds are not symmetrical and the P—OH distances (av. 1·578 Å) are significantly longer than the P—O distances (av. 1·493 Å). The phosphate geometry was compared with $H_2PO_4^-$ groups in other structures by calculating the distortion indices (Baur, 1970, 1974). The values of these indices* for $Ba(H_2PO_4)_2$ are characteristic of acid phosphates where two O atoms coordinate to the same divalent cation. The $H_2PO_4^-$ geometry is very similar to that of the phosphate groups with shared edges in the two $Ca(H_2PO_4)_2$ structures mentioned above.

Support of this research by the National Science Foundation (DMR 24613) and Vanderbilt University is gratefully acknowledged. We also thank Mr Gary Carnahan for technical assistance.

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* Values ($\times 10^3$) are: DI(PO) = 28, DI(OPO) = 44, DI(OO) = 22, DI(PO) = 17.

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