

## Barium tetrphosphate

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The structure of the low-temperature form of barium tetrphosphate,  $\text{Ba}_3\text{P}_4\text{O}_{13}$ , shows the tetrphosphate to exist in an *S* conformation.

## Comment

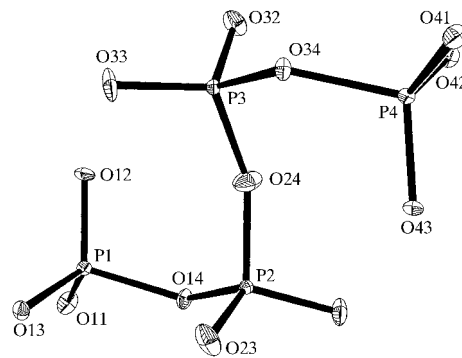
In 1986, Millet *et al.* (1986) reported unit-cell dimensions for low- and high-temperature forms of  $\text{Ba}_3\text{P}_4\text{O}_{13}$ . The low-temperature form (triclinic space group  $P1$  or  $P\bar{1}$ ;  $a = 5.757$ ,  $b = 7.243$ ,  $c = 8.104$  Å,  $\alpha = 82.75$ ,  $\beta = 73.94$ ,  $\gamma = 70.71^\circ$ ) transforms at 1143 K into the high-temperature form (orthorhombic space group  $Pbcm$ ;  $a = 7.107$ ,  $b = 13.883$ ,  $c = 19.219$  Å) (cell dimensions from precession camera data).

Gatehouse *et al.* (1991) later reported the crystal structure of the low-temperature form in the triclinic space group  $P\bar{1}$  [ $a = 5.691$  (5),  $b = 7.238$  (7),  $c = 8.006$  (5) Å,  $\alpha = 83.65$  (5),  $\beta = 75.95$  (8),  $\gamma = 70.49$  (7)°]. The asymmetric unit consisted of two Ba atoms and a linear tetrphosphate group ( $\text{P}_4\text{O}_{13}$ ) chain, with one Ba atom and the central O atom of the  $\text{P}_4\text{O}_{13}$  chain existing on a center of symmetry. Disorder of the central bridging O atom and of the two terminal O atoms on adjacent P atoms led to an incomplete refinement. Only the Ba atoms were refined anisotropically, while the P and O atoms were refined with isotropic displacement parameters.

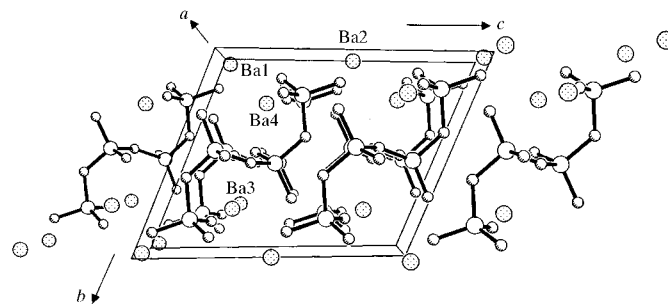
We have isolated crystals of the low-temperature form of  $\text{Ba}_3\text{P}_4\text{O}_{13}$  and refined single-crystal data in a triclinic cell of doubled volume [600.65 (12) Å]. We find the disorder evident in the  $\text{P}_4\text{O}_{13}$  group seen in the triclinic cell of volume 301 Å to be completely absent in our refinement. Moreover, the central bridging O atom shows a normal P—O—P angle of 151.4 (4) Å.

The  $\text{P}_4\text{O}_{13}$  group has an *S* conformation (Fig. 1), as is common (Averbuch-Pouchot, 1987; Averbuch-Pouchot & Durif, 1987), and not a *U* conformation (Lii *et al.*, 1989). The P···P···P···P torsion angle is 179.1 (5)°, which is consistent with this assignment. The four P atoms are coplanar (r.m.s. deviation = 0.012). The relative O-atom conformations are pseudo-eclipsed about the P1···P2 direction, pseudo-stag-

gered about the P2···P3 direction and pseudo-eclipsed about the P3···P4 line. Average O—P···P—O torsion angles about the three P···P directions are 9.8, 56.1 and 30.6°, respectively, further evidence of the need to refine the O atoms of the  $\text{P}_4\text{O}_{13}$  group without constrained symmetry. The angles at the bridging O atoms are 128.6 (3), 151.4 (4) and 130.0 (3)°.



**Figure 1**  
A view of the  $\text{P}_4\text{O}_{13}$  group of the title compound. Displacement ellipsoids are shown at the 50% probability level.



**Figure 2**  
Projection of  $\text{Ba}_3\text{P}_4\text{O}_{13}$  on to the 011 plane.

The four Ba atoms appear related by the pseudosymmetry element  $(\frac{1}{2} + x, y, \frac{1}{2} + z)$ . Atoms Ba1 and Ba2 exist on a center of symmetry and are eight-coordinate, with Ba—O distances in the range 2.659 (4)–3.113 (5) Å for Ba1 and 2.719 (4)–2.938 (4) Å for Ba2 (Table 1). Atom Ba3 is seven-coordinate [Ba—O 2.662 (4)–2.891 (4) Å], while atom Ba4 has eight O-atom neighbors within the distance range 2.680 (4)–3.194 (4) Å.

Ba atoms are seen in two tunnels extending in the [100] direction. These tunnels differ in their placement in the curves of the  $\text{P}_4\text{O}_{13}$  groups (Ba3 and Ba4) or at the ends of such groups (Ba1 and Ba2) (Fig. 2).

## Experimental

Crystals of  $\text{Ba}_3\text{P}_4\text{O}_{13}$  were obtained from a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{BaCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  (proportion 2:1:2), which was ground in an agate mortar and then heated in a porcelain crucible from 373 to 873 K. A quantity of  $(\text{NH}_4)_2\text{HPO}_4$  equal to 10% of the final mass was added to the top of the crucible and the material then heated to fusion (1173 K). Colorless crystals were found in the product after controlled cooling (6 K h<sup>-1</sup>) to 673 K.

## Crystal data

Ba <sub>3</sub> P <sub>4</sub> O <sub>13</sub>	Z = 2
M <sub>r</sub> = 743.90	D <sub>x</sub> = 4.113 Mg m <sup>-3</sup>
Triclinic, P $\bar{1}$	Mo K $\alpha$ radiation
a = 7.557 (1) Å	Cell parameters from 23 reflections
b = 8.618 (1) Å	$\theta$ = 6.2–12.8°
c = 10.582 (1) Å	$\mu$ = 10.33 mm <sup>-1</sup>
$\alpha$ = 108.26 (1)°	T = 293 (2) K
$\beta$ = 104.50 (1)°	Plate, colorless
$\gamma$ = 102.37 (1)°	0.15 × 0.15 × 0.15 mm
V = 600.65 (12) Å <sup>3</sup>	

## Data collection

Syntex P4 four-circle diffractometer	R <sub>int</sub> = 0.022
$\theta/2\theta$ scans	$\theta_{\max}$ = 30.0°
Absorption correction: $\psi$ scan (XEMP; Siemens, 1990)	h = -10 → 1
T <sub>min</sub> = 0.72, T <sub>max</sub> = 0.78	k = -11 → 11
4118 measured reflections	l = -14 → 14
3397 independent reflections	3 standard reflections
2777 reflections with I > 2 $\sigma$ (I)	every 97 reflections
	intensity decay: none

## Refinement

Refinement on F <sup>2</sup>	w = 1/[ $\sigma^2(F_o^2) + (0.0592P)^2 + 5.8638P$ ]
R(F) = 0.032	where P = (F <sub>o</sub> <sup>2</sup> + 2F <sub>c</sub> <sup>2</sup> )/3
wR(F <sup>2</sup> ) = 0.099	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
S = 0.90	$\Delta\rho_{\max}$ = 0.03 e Å <sup>-3</sup>
3397 reflections	$\Delta\rho_{\min}$ = -0.08 e Å <sup>-3</sup>
185 parameters	Extinction correction: SHELXL97
	Extinction coefficient: 0.0173 (7)

Data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1990); software used to prepare material for publication: SHELXL97.

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**Table 1**

Selected interatomic distances (Å).

Ba1–O33 <sup>i</sup>	2.659 (4)	Ba3–O33 <sup>vi</sup>	2.891 (4)
Ba1–O13 <sup>i</sup>	2.699 (4)	Ba3–O11 <sup>i</sup>	3.268 (5)
Ba1–O41	2.742 (4)	Ba3–Ba2 <sup>vii</sup>	4.4559 (6)
Ba1–O12 <sup>j</sup>	3.113 (5)	Ba4–O23 <sup>viii</sup>	2.680 (4)
Ba1–O43	3.325 (4)	Ba4–O41 <sup>iv</sup>	2.682 (4)
Ba2–O42 <sup>ii</sup>	2.719 (4)	Ba4–O12 <sup>vi</sup>	2.700 (4)
Ba2–O22 <sup>ii</sup>	2.740 (4)	Ba4–O32 <sup>vi</sup>	2.739 (4)
Ba2–O11 <sup>iii</sup>	2.772 (4)	Ba4–O13 <sup>viii</sup>	2.777 (4)
Ba2–O43 <sup>ii</sup>	2.938 (4)	Ba4–O22 <sup>ii</sup>	2.799 (4)
Ba3–O32 <sup>iv</sup>	2.662 (4)	Ba4–O42 <sup>ix</sup>	2.876 (4)
Ba3–O11 <sup>v</sup>	2.671 (4)	Ba4–O41 <sup>ix</sup>	3.194 (4)
Ba3–O43	2.674 (4)	Ba4–P4 <sup>ix</sup>	3.5171 (14)
Ba3–O23	2.771 (5)	Ba4–P3 <sup>vi</sup>	3.6111 (14)
Ba3–O42 <sup>iv</sup>	2.779 (4)	Ba4–Ba1 <sup>iv</sup>	4.3980 (6)
Ba3–O13 <sup>i</sup>	2.890 (4)		

Symmetry codes: (i) x, 1 + y, z; (ii) x - 1, y, z - 1; (iii) x - 1, 1 + y, z - 1; (iv) x - 1, y, z; (v) 1 - x, -1 - y, 1 - z; (vi) 1 - x, -1 - y, -z; (vii) x, y, 1 + z; (viii) -x, -1 - y, -z; (ix) 1 - x, -y, -z.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1147). Services for accessing these data are described at the back of the journal.

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