

Crystal structure of barium cyclotriphosphate tetrahydrate, $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$

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Abstract. $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ is monoclinic, $C2/m$, with $a = 16.09(1)$, $b = 8.368(5)$, $c = 7.717(3)$ Å, $\beta = 95.38(5)^\circ$, $V = 1034,6$ Å³, $Z = 2$ and $D_x = 3.074$ g/cm⁻³. The structure has been solved using 1489 independent data with a final R value of 0.038. The P_3O_9 ring anions have a mirror symmetry. All barium atoms are in the mirror planes. Two of them are located in a fourfold position and are statistically distributed in a wide elongated centrosymmetrical cavity.

Introduction

Barium cyclotriphosphate hexahydrate: $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$ was first characterized by Martin (1972). Later on, its crystal structure has been determined by Masse et al. (1976). Up to now no other hydrate has been described for this salt. In the present work we report chemical preparation and crystal structure of the tetrahydrate $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$.

Chemical preparation

Chemical preparation of pure $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ has been difficult to optimize.

Various compounds can be obtained when adding a water solution of BaCl_2 to a water solution of $\text{Na}_3\text{P}_3\text{O}_9$. Results are mainly dependent of the respective concentrations of the solutions and of the Ba/Na ratios. Preparation of $\text{BaNaP}_3\text{O}_9 \cdot 4\text{H}_2\text{O}$ by using dilute solutions of $\text{Na}_3\text{P}_3\text{O}_9$ and BaCl_2 or $\text{Ba}(\text{NO}_3)_2$ has been previously described by Martin and

Durif (1972). When solutions are more concentrated the results are quite different:

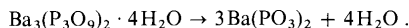
a) If a solution of 15 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 35 cm³ water is added slowly and without any stirring to a solution of 3 g $\text{Na}_3\text{P}_3\text{O}_9$ in 25 cm³ water ($\text{Ba}/\text{Na} \sim 2$) one observes almost immediately the formation of a large amount of small tufts of lath like needles¹. After filtration to eliminate the mother liquor, an equivalent volume of water is added to this solid phase which within a few minutes is transformed into minute crystals of $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$. No contamination is observed.

b) If the same quantities of starting materials are dissolved in 50 cm³ water and again mixed without any stirring one observes after some hours the formation of large crystals of the tetrahydrate. In this case the preparation is often contaminated by 10 to 20% of large elongated prisms of the hexahydrate.

c) If the concentration of the starting solutions is lowered (3 g $\text{Na}_3\text{P}_3\text{O}_9$ in 100 cm³ water, 15 g BaCl_2 in 100 cm³ water), large crystals of the hexahydrate are formed within a day, without any contamination.

All the experiments reported here have been run at room temperature.

Crystals of $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ are stout monoclinic prisms. Firing at 600 °C for some hours leads to the barium polyphosphate:



Crystals of $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ are stable for months at room temperature.

Crystal chemistry

A preliminary study by the Weissenberg method showed the title compound to be monoclinic, $C2$, Cm or $C2/m$. A refinement of the cell parameters made during the intensity data collection with 18 reflexions ($10 < \theta < 12^\circ$) leads to $a = 16.09(1)$, $b = 8.368(5)$, $c = 7.717(5)$ Å and $\beta = 9538(5)^\circ$. There are two formula units per cell. The crystal structure determination will prove $C2/m$ to be the proper space group.

Crystal structure determination

The experimental conditions used during intensity data collection and various physical data are reported in Table 1. Classical methods were used for the structure determination: three-dimensional Patterson and successive Fourier syntheses. Hydrogen atoms could not be located. After the last refinement cycles using anisotropic thermal parameters the R value

¹ A not yet identified addition compound of barium chloride and sodium cyclotriphosphate

Table 1. Parameters used for the X-ray data collection

Apparatus:	Philips PW 1100	Scan width:	1.40°
Wave length:	$\text{AgK}\alpha(0.5608 \text{ \AA})$	Scan speed:	0.02 °s ⁻¹
Monochromator:	Graphite plate		multiple scans for weak reflexions
Scan mode:	$\theta/2\theta$	Number of collected reflexions:	2063 ($\pm H, K, L$)
Theta range:	3–25°		$H_{\text{max}} = 28$ $K_{\text{max}} = 14$ $L_{\text{max}} = 11$
Crystal size:	0.14 × 0.16 × 0.16 mm ³	Total background measuring time:	20 s
μ :	32.9 cm ⁻¹	Reference reflexions:	040 and 0 $\bar{4}$ 0
$F(000)$; M_w :	884; 957.91		

Table 2. Final atomic coordinates and B_{eq} . $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \bar{a}_i \cdot \bar{a}_j \cdot \beta_{ij}$

Atoms	x	y	z	$B_{\text{eq}}[\text{Å}^2]$
Ba(1)	0.19029(3)	0	0.95150(7)	1.20(1)
Ba(2)	0.04701(6)	0	0.4317(1)	1.21(2)
P(1)	0.13574(9)	0.3311(2)	0.7000(2)	1.11(3)
P(2)	0.3080(1)	0	0.5976(3)	1.36(5)
O(L12)	0.1545(3)	0.3507(5)	0.4997(5)	1.46(9)
O(E11)	0.2143(3)	0.3147(6)	0.8157(6)	1.7(1)
O(E12)	0.0735(3)	0.2025(6)	0.7069(6)	1.7(1)
O(L)	0.0926(4)	$\frac{1}{2}$	0.7327(8)	1.3(1)
O(E21)	0.3465(5)	0	0.7812(9)	2.1(2)
O(E22)	0.2158(5)	0	0.575(1)	2.7(2)
O(W)	0.0788(4)	0.2067(9)	0.1154(8)	3.8(2)

converged to 0.038 for a set of 1489 reflections corresponding to $|F_o| > 4 \sigma(F_o)$. All along the structure determination a unitary weighting scheme has been applied. Table 2 reports the final atomic coordinates and B_{eq} . A list of anisotropic thermal coefficients has been deposited².

Description of the structure

The Figure 1 shows a projection of the atomic arrangement along the \bar{c} axis onto the (a, b) -plane.

² Additional material to this paper can be ordered referring to the no. CSD 51753, name(s) of the author(s) and citation to the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

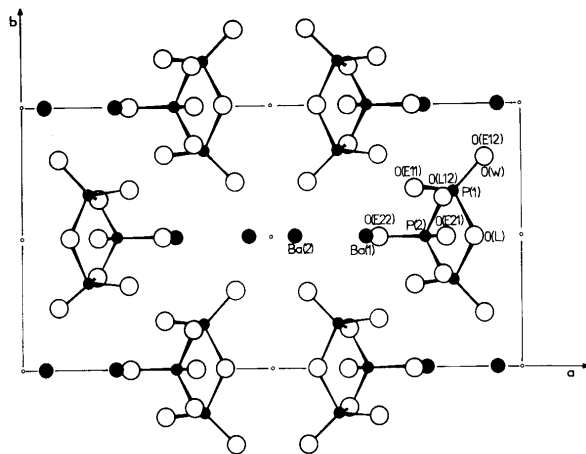


Fig. 1. Projection of the atomic arrangement of $\text{Ba}_3(\text{P}_3\text{O}_9)_2 \cdot 4\text{H}_2\text{O}$ along the z axis onto the (a,b) -plane. O(E12) and O(W) are superimposed in projection

The P_3O_9 ring anion

As one of the phosphorus atoms of the ring anion [P(2)] is located on the mirror plane, this ring is built up by only two independent phosphorus atoms and adopts a mirror symmetry. Main interatomic distances and bond angles in the ring are reported in Table 3. Bond lengths and angles within this P_3O_9 group are not fundamentally different from those found in similar ring anions. The P–O distances corresponding to the bridging oxygen atoms are significantly longer ($\text{P}=\text{O} = 1.606 \text{ \AA}$) than those corresponding to the external oxygen atoms ($\text{P}=\text{O} = 1.482 \text{ \AA}$), while the P–P–P angles are very close by those of a perfectly regular P_3O_9 anion (60.97 and 58.06°). Only external oxygen atoms of the ring are bonded to barium atoms.

Barium atoms

All barium atoms are located in the mirror plane, but their environment is very different. The four Ba(1) atoms have a tenfold coordination made by eight oxygen atoms and two water molecules, with Ba–O distances ranging from 2.733 to 3.050 \AA . The other two barium atoms [Ba(2)] are statistically distributed $\text{SOF}(\text{Ba}) = 0.500(4)$ on a fourfold position and are located in a large oblongue centrosymmetrical cavity. They have a sevenfold coordina-

Table 3. Main interatomic distances [\AA] and bond angles [$^\circ$] in the P_3O_9 ring anion

P(1)O ₄ tetrahedron		P(2)O ₄ tetrahedron	
P(1)	O(L12)	P(2)	O(L12)
O(L12)	1.611(3)	O(E21)	1.492(6)
O(E11)	1.112(2)	O(E22)	1.478(6)
O(E12)	1.073(2)	O(L12)	1.133(2)
O(L)	1.006(2)	O(L12)	1.077(2)
(2 ×) P(1)–P(2)	2.912(2) \AA		
P(1)–P(1)	2.826(2)		
		P(1)–P(1)–P(2)	60.97(3) $^\circ$
		P(1)–P(2)–P(1)	58.06(5)

Table 4. Main interatomic distances [\AA] in BaO_n polyhedra

Ba(1)O ₁₀ polyhedron		Ba(2)O ₇ polyhedron	
Ba(1)–O(E11)	Ba(1)–O(E12)	Ba(2)–O(E12)	Ba(2)–O(W)
Ba(1)–O(E11)	2.874(3) ($\times 2$)	Ba(2)–O(E12)	2.719(3) ($\times 2$)
Ba(1)–O(E11)	2.733(3) ($\times 2$)	Ba(2)–O(W)	2.836(6)
Ba(1)–O(W)	2.869(5) ($\times 2$)	Ba(2)–O(W)	3.073(7) ($\times 2$)
		Ba(1)–O(E12)	2.718(3) ($\times 2$)
		Ba(1)–O(E12)	2.718(3) ($\times 2$)
		Ba(1)–O(E12)	3.050(3) ($\times 2$)

tion built up by five oxygen atoms and two water molecules with Ba–O distances ranging from 2.718 to 3.073 Å.

The statistical occupation of a crystallographic position by an associated cation is not common in the crystal chemistry of condensed phosphates. Up to now the only example is given by the $\text{LnM}^{\text{I}}\text{P}_4\text{O}_{12}$ series where 12 M^{I} atoms are located on the 16(c) position of the $I43d$ space group (Rzaigui et al., 1983).

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