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## Structure of Low-Ba<sub>3</sub>P<sub>4</sub>O<sub>13</sub>

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**Abstract.** Ba<sub>3</sub>P<sub>4</sub>O<sub>13</sub>,  $M_r = 743.88$ , triclinic,  $P\bar{1}$ ,  $a = 5.691$  (5),  $b = 7.238$  (7),  $c = 8.006$  (5) Å,  $\alpha = 83.65$  (5),  $\beta = 75.95$  (8),  $\gamma = 70.49$  (7)°,  $V = 301.4$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 4.10$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 10.29$  mm<sup>-1</sup>,  $F(000) = 332$ ,  $T = 293$  K, final  $R = 0.039$  for 1222 counter-measured reflections. The structure comprises Ba<sup>2+</sup> ions and non-centrosymmetric [P<sub>4</sub>O<sub>13</sub>]<sup>6-</sup> polyanions consisting of four corner-shared phosphorus–oxygen tetrahedra with a P—P—P torsion angle of 180°. The mean P—O and Ba—O distances are 1.53 and 2.77 Å respectively.

**Introduction.** The structures of a number of compounds in the BaO–P<sub>2</sub>O<sub>5</sub> system have been reported; however, only the unit-cell dimensions of the low- and high-temperature forms of Ba<sub>3</sub>P<sub>4</sub>O<sub>13</sub> were first given by Millet, Parker & Roth (1986). The structure of the low-temperature form (low-) of Ba<sub>3</sub>P<sub>4</sub>O<sub>13</sub> is reported here.

**Experimental.** A colourless crystal fragment with approximate faces  $\bar{1}\bar{1}\bar{1}$ , 111,  $0\bar{1}0$ , 010,  $10\bar{2}$ , and  $1\bar{1}3$  and dimensions  $0.035 \times 0.035 \times 0.065$  mm, was selected from a preparation described elsewhere (Millet, Parker & Roth, 1986) and mounted on a silica capillary using 'Tyton 5 Minit' adhesive. Crystal data obtained using a Philips PW 1100 computer-controlled four-circle diffractometer equipped with a graphite monochromator. Cell parameters obtained as the means of 10 measurements made on the positions of 24 reflections  $13 < 2\theta < 38^\circ$  as orientation checks during data collection. Data collected

out to  $2\theta(\text{Mo } K\alpha) = 60^\circ$  using the  $\omega$ -scan technique with a symmetric scan range of  $\pm(0.65 + 0.3\tan\theta)^\circ$  in  $\omega$  from the calculated Bragg angle, at a scan rate of  $0.04^\circ \text{ s}^{-1}$ . No reflection was sufficiently intense to require the insertion of an attenuation filter. 1751 unique reflections measured to  $2\theta = 60^\circ$ , 1222 unique reflections [ $I > 3\sigma(I)$ ] used in analysis,  $R_{\text{int}} = 0.042$ ; index range  $h = 11/11$ ,  $k = 10/7$ ,  $l = 0/10$ . Three standard reflections measured at 3 h intervals; no decomposition occurred. Data processed using the program written specifically for the Philips PW 1100 diffractometer (Hornstra & Stubbe, 1972). Absorption correction applied, max. and min. transmission factors 0.7727 and 0.6861, respectively. No extinction correction necessary. The Ba atom located by inspection on the origin, remaining atoms located in subsequent difference Fourier syntheses. Function minimized in full-matrix least-squares refinement on  $F$ ,  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  is the weight  $[\sigma^2(F_o)]^{-1}$ . During refinement O(7), on a centre of symmetry showed peaks in the difference synthesis consistent with disorder in such a way that the P—O—P angle about it departed from 180°. In addition O(5) and O(6) showed signs of disorder in the difference synthesis consistent with the O(7) disorder, indicating a small rotational disorder of the P(1) tetrahedron about the O(3)—P(1) bond. Each of the O(5) and O(6) atoms has been refined as two atoms with 50% occupancies and O(7) has been moved off the centre of symmetry. Ba and P atoms refined anisotropically, other atoms refined isotropically; 60 variable parameters, final  $R = 0.039$  and  $wR = 0.042$  (for observed reflections); max.  $\Delta/\sigma$  in final cycle 0.005. Final difference synthesis had  $\Delta\rho$  within 1.3 and  $-1.3 \text{ e } \text{Å}^{-3}$ , in vicinity of P(1) and O(6'). Scattering

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Table 1. Atomic parameters for low-Ba<sub>3</sub>P<sub>4</sub>O<sub>13</sub> with e.s.d.'s in parentheses

	x	y	z	U <sub>iso</sub> (Å <sup>2</sup> )
Ba(1)*	0.0	0.0	0.0	
Ba(2)*	0.64644 (11)	-0.41221 (8)	-0.77426 (7)	
P(1)	-0.0091 (4)	0.2094 (3)	-0.4688 (3)	0.0098 (4)
P(2)	0.3335 (4)	0.1936 (3)	-0.8069 (3)	0.0094 (4)
O(1)	0.1088 (12)	0.2985 (10)	-0.8905 (8)	0.015 (1)
O(2)	0.5473 (13)	0.2833 (10)	-0.8710 (9)	0.018 (2)
O(3)	0.2304 (12)	0.2433 (10)	-0.6022 (8)	0.014 (1)
O(4)	0.4145 (14)	-0.0258 (11)	-0.8146 (9)	0.023 (2)
O(5)	0.0015 (32)	0.2504 (25)	-0.2870 (20)	0.018 (3)
O(5')	0.0582 (31)	0.1853 (24)	-0.3039 (19)	0.016 (3)
O(6)	-0.2552 (30)	0.3121 (24)	-0.5156 (20)	0.020 (3)
O(6')	-0.2353 (26)	0.3728 (22)	-0.4962 (18)	0.012 (3)
O(7)	-0.0504 (23)	0.0236 (19)	-0.5341 (15)	0.011 (3)

\* Anisotropic thermal parameters are of the form  $\exp[2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ :

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Ba(1)	0.0131 (4)	0.0091 (4)	0.0123 (4)	-0.0037 (3)	-0.0047 (3)	0.0004 (3)
Ba(2)	0.0104 (3)	0.0088 (3)	0.0117 (3)	-0.0035 (2)	-0.0001 (2)	-0.0007 (2)

factors for neutral atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations performed on the Monash University VAX 11/780 computers; the major program used was *SHELX76* (Sheldrick, 1976).

Final parameters and their e.s.d.'s are given in Table 1.\* Selected bond lengths and angles are given in Table 2.

**Discussion.** The structure consists of Ba<sup>2+</sup> cations and [P<sub>4</sub>O<sub>13</sub>]<sup>6-</sup> polyanions (Fig. 1). The polyanion is non-centrosymmetric (coplanar P atoms) and can be seen in Fig. 2 linking the two barium polyhedra – the O atom disorder is not shown. The P–P distances in the polyanion are P(1)–P(2) 2.914 (3) and P(1)–P(1) 3.087 (8) Å and the P(2)–P(1)–P(1)–P(2) torsion angle is 180°.

The P–O bond distances range from 1.44 (2)–1.637 (7) Å [mean 1.54 (6) Å]. The average bridging P–O distance [1.61 (3) Å] is greater than the average terminal P–O distance [1.49 (4) Å]. For comparison the mean P–O bridging and terminal distances are given in Table 3 for six other compounds containing [P<sub>4</sub>O<sub>13</sub>]<sup>6-</sup> polyanions together with those for Ba<sub>3</sub>P<sub>4</sub>O<sub>13</sub> determined here. The involvement of the non-bridging O atoms in bonds to barium is reflected in the greater terminal P–O distances. In addition the P–P–P–P torsion angles are given from which it can be seen that with the exception of P<sub>4</sub>O<sub>13</sub><sup>6-</sup> in Cr<sub>2</sub>P<sub>4</sub>O<sub>13</sub> (Lii, Chen, Su & Wang, 1989) the P<sub>4</sub>O<sub>13</sub><sup>6-</sup> polyanions have torsion angles > 170.4°, all resembling four-tetrahedra chains rather than U-shaped

Table 2. Distances (Å) and selected bond angles (°)

P(1)—O(5')	1.439 (17)	P(1)—O(3)	1.587 (7)
—O(6)	1.467 (16)	—O(7)	1.601 (16)
—O(6')	1.472 (13)	—O(7) <sup>e</sup>	1.604 (14)
—O(5)	1.537 (18)		
P(2)—O(4)	1.502 (8)	P(2)—O(2)	1.522 (9)
—O(1)	1.522 (7)	—O(3)	1.637 (7)
Barium contacts out to 3.2 Å			
Ba(1)—O(5')	2.648 (15) × 2	Ba(1)—O(5)	2.765 (16) × 2
—O(1) <sup>a,h</sup>	2.719 (8) × 2	—O(4) <sup>a,h</sup>	3.024 (9) × 2
—O(2) <sup>c,d</sup>	2.749 (6) × 2		
Ba(2)—O(6') <sup>e</sup>	2.663 (14)	Ba(2)—O(6) <sup>e</sup>	2.767 (14)
—O(2) <sup>f</sup>	2.683 (14)	—O(1) <sup>f</sup>	2.781 (6)
—O(4)	2.685 (7)	—O(5) <sup>f</sup>	2.792 (2)
—O(6') <sup>e</sup>	2.734 (13)	—O(1) <sup>g</sup>	2.878 (6)
—O(6) <sup>f</sup>	2.736 (16)	—O(5') <sup>d</sup>	2.915 (21)
O(6)—P(1)—O(5)	114.3 (8)	O(5')—P(1)—O(6')	118.8 (8)
O(6)—P(1)—O(3)	114.4 (7)	O(5')—P(1)—O(3)	104.8 (8)
O(6)—P(1)—O(7)	82.5 (9)	O(5')—P(1)—O(7)	116.1 (9)
O(5)—P(1)—O(7) <sup>e</sup>	104.0 (8)	O(6')—P(1)—O(3)	107.0 (6)
O(3)—P(1)—O(7)	103.6 (5)	O(6')—P(1)—O(7)	103.5 (8)
O(5)—P(1)—O(3)	108.9 (8)	O(3)—P(1)—O(7)	105.8 (5)
O(4)—P(2)—O(1)	113.2 (5)	O(1)—P(2)—O(2)	110.7 (4)
O(4)—P(2)—O(2)	115.2 (4)	O(1)—P(2)—O(3)	105.8 (3)
O(4)—P(2)—O(3)	105.9 (4)	O(2)—P(2)—O(3)	105.1 (4)
P(1)—O(7)—P(1) <sup>e</sup>	149.2 (9)		

Symmetry codes: (a)  $-x, -y, -z-1$ ; (b)  $x, y, 1+z$ ; (c)  $x-1, y, z+1$ ; (d)  $1-x, -y, -z-1$ ; (e)  $1+x, -1+y, z$ ; (f)  $x, y-1, z$ ; (g)  $1-x, -y, -2-z$ .

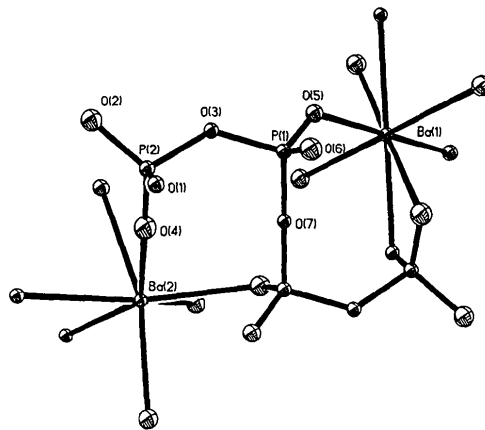
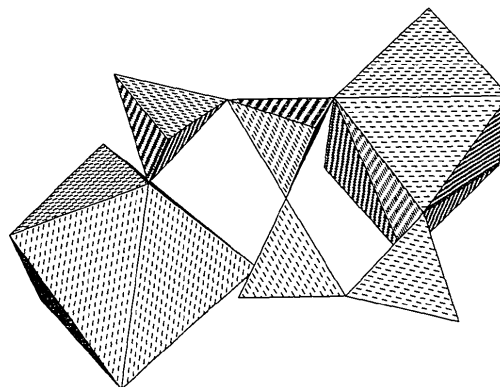
Fig. 1. The structure comprising Ba<sup>2+</sup> cations and [P<sub>4</sub>O<sub>13</sub>]<sup>6-</sup> polyanions, with the atom labeling.

Fig. 2. The polyanion linking two barium polyhedra.

\* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54304 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Compounds containing tetraphosphate ions*

	Mean P—O (Å)	Mean P—O (Å)	P—P—P (°)	Ref.
	Bridging	Terminal	Torsion angle	
Cr <sub>2</sub> P <sub>4</sub> O <sub>13</sub>	1.59 (1)	1.50 (3)	70.98	<i>a</i>
Ca(Nb <sub>2</sub> O)(P <sub>4</sub> O <sub>13</sub> ) (P <sub>2</sub> O <sub>7</sub> )	1.59 (2)	1.49 (5)	170.4	<i>b</i>
(NH <sub>4</sub> ) <sub>2</sub> SiP <sub>4</sub> O <sub>13</sub>	1.60 (2)	1.50 (3)	177.3	<i>c</i>
Pb <sub>3</sub> P <sub>4</sub> O <sub>13</sub>	1.60 (3)	1.51 (2)	177.4	<i>d</i>
(NbO) <sub>2</sub> P <sub>4</sub> O <sub>13</sub>	1.58 (10)	1.49 (8)	−178.7	<i>e</i>
	1.56 (6)	1.50 (6)	178.9	
Bi <sub>2</sub> P <sub>4</sub> O <sub>13</sub>	1.58 (2)	1.51 (1)	180	<i>f</i>
Low-Ba <sub>3</sub> P <sub>4</sub> O <sub>13</sub>	1.61 (3)	1.49 (4)	180	<i>g</i>

References: (a) Lii, Chen, Su & Wang (1989); (b) Averbuch-Pouchot (1987); (c) Durif, Averbuch-Pouchot & Guitel (1976); (d) Averbuch-Pouchot & Durif (1987); (e) Nikolaev, Sadikov, Lavrov & Porai-Koshits (1986); (f) Bagieu-Beucher & Averbuch-Pouchot (1987); (g) this work.

ions. A similar situation was commented on recently (Gatehouse, Guddat & Roth, 1987) for E<sub>4</sub>O<sub>13</sub><sup>7−</sup> ions where for Na<sub>14</sub>Al<sub>4</sub>O<sub>13</sub> (Griesfeller, Kohler & Hoppe, 1983) the torsion angle is 180°, in Ag<sub>10</sub>Si<sub>4</sub>O<sub>13</sub> (Jansen & Keller, 1979) it is 177.4 (2)° and in Rb<sub>2</sub>Cr<sub>4</sub>O<sub>13</sub> (Löfgren, 1973) it is 172.30 (5)°, whereas in Ba<sub>3</sub>V<sub>4</sub>O<sub>13</sub> the V—V—V—V torsion angle is 56.07 (6)° and the polyanion is U-shaped as in Cr<sub>2</sub>P<sub>4</sub>O<sub>13</sub>.

On the basis of geometric and bond-distance considerations, the coordination numbers for the barium ions have been taken to be eight for Ba(1) and seven for Ba(2). The coordination polyhedron of Ba(1) is best described, in terms of the criteria of King (1969, 1970) as programmed by Johnson, Taylor & Cox (1980), as a 'distorted cube' with Ba—O distances ranging from 2.72 (1)–3.025 (8) Å [mean 2.82 (13) Å]

and that of Ba(2) as a 'four-capped trigonal prism' with the Ba—O distances ranging from 2.68 (1)–2.877 (6) Å [mean 2.76 (7) Å].

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## Structure of Two Modifications of Dysprosium Sesquisulfide, Dy<sub>2</sub>S<sub>3</sub>

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**Abstract.** Dy<sub>2</sub>S<sub>3</sub> (A), U<sub>2</sub>S<sub>3</sub> type structure, *M<sub>r</sub>* = 421.18, orthorhombic, *Pnma*, *a* = 10.609 (1), *b* = 3.864 (1), *c* = 10.429 (1) Å, *V* = 427.5 (1) Å<sup>3</sup>, *Z* = 4,

*D<sub>x</sub>* = 6.543 g cm<sup>−3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 362.2 cm<sup>−1</sup>, *F*(000) = 720, *T* = 298 K, *R<sub>F</sub>* = 0.023 for 947 observed reflections with *I* > 2.5σ(*I*). All atoms at 4(c). Two types of Dy. Dy(1) is coordinated by seven S atoms at a short distance approximately in a

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