In our earlier paper (Łukaszewicz *et al.*, 1983) we reported that in some crystals of NH_4BeF_3 grown from the same mother solution phase II was missing, which we attributed to differences in crystal perfection and the distribution of defects. The intermediate phase II was also not found by Makita & Suzuki (1980), Yoshida, Tsukamoto, Futama & Makita (1984) or Yoshida, Takemasa, Oshino & Makita (1984). It should be added that the transition at 526 K reported by Yoshida, Tsukamoto *et al.* (1984) and Yoshida, Takemasa *et al.* (1984) is not connected with an additional phase transition but corresponds to decomposition of the compound. Thermogravimetric analysis (Fig. 3) performed on an Elmer–Perkin gravimeter shows that at 471 K a loss of weight of sample starts according to the scheme: $NH_4BeF_3 \rightarrow NH_4F + BeF_2$. This effect was also observed on the DSC curve where a broad and irregular peak, typical for decomposition of the substance, was recorded at the same temperature.

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References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Czapla, Z., Czupiński, O. & Waśkowska, A. (1982). *J. Phys. Soc. Jpn*, **51**, 2693–2694.
Łukaszewicz, K., Waśkowska, A., Tomaszewski, P. E. & Czapla, Z. (1983). *Phase Transitions*, **4**, 47–54.
Makita, Y. & Suzuki, S. (1980). *J. Phys. Soc. Jpn*, **48**, 693–694.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Waśkowska, A. (1983). *Acta Cryst.* C**39**, 1167–1169.
Yoshida, H., Takemasa, H., Oshino, Y. & Makita, Y. (1984). *J. Phys. Soc. Jpn*, **53**, 2600–2605.
Yoshida, H., Tsukamoto, T., Futama, H. & Makita, Y. (1984). *J. Phys. Soc. Jpn*, **53**, 2606–2612.

Acta Cryst. (1985). C**41**, 1717–1718

Structure of Tribarium Dibismuth Tetrakis(phosphate)

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Abstract. $Ba_3Bi_2(PO_4)_4$, $M_r = 1209{\cdot}87$, monoclinic, $C2/c$, $a = 20{\cdot}298$ (20), $b = 8{\cdot}730$ (3), $c = 8{\cdot}766$ (3) Å, $\beta = 109{\cdot}98$ (6)°, $V = 1460{\cdot}0$ (7) Å^3, $Z = 4$, $D_x = 5{\cdot}504$ Mg m^{-3}, Ag $K\alpha_1$, $\lambda = 0{\cdot}56083$ Å, $\mu = 176{\cdot}7$ cm^{-1}, $F(000) = 2088$, $T = 293$ K, $R = 0{\cdot}038$, 3036 unique reflections. Isolated PO_4 tetrahedra determine irregular coordinations around Ba and Bi atoms. The sites of Ba(1) and Ba(2) have eightfold coordination with a more regular arrangement around Ba(2), which is in a special position. The Bi atom has seven oxygen neighbours in a distorted arrangement.

Introduction. The monophosphate $Ba_3Bi_2(PO_4)_4$ was prepared starting from a $Ba(PO_3)_2$,$2Bi_2O_3$ mixture, melted at 1373 K and cooled slowly to 1173 K and then rapidly to room temperature. The initial aim was to obtain a chemical compound with the BiO_5 pyramidal arrangement.

Experimental. Thick platelet: $0{\cdot}16 \times 0{\cdot}24 \times 0{\cdot}24$ mm. Weissenberg photographs and data collection indicate monoclinic symmetry (hkl, $h+k = 2n$ and $h0l$, $l = 2n$) compatible with space groups Cc and $C2/c$; cell constants from 20 reflections ($10 < \theta_r < 13°$) using a four-circle Philips PW 1100 diffractometer. Graphite-monochromated Ag $K\alpha$, $\omega/2\theta$ scan, scan width 1·2°, scan speed 0·02° s^{-1}. θ range 3 to 35°. $\pm h,k,l$, $h_{max} = 45$, $k_{max} = 30$, $l_{max} = 30$. Intensity reference reflections 060 and 462. 4985 independent reflections collected. 3036 ($F_o > 2\sigma_F$) used to refine structure until $R = 0{\cdot}038$, $wR = 0{\cdot}048$; unit weights; full-matrix refinement on F; no absorption correction; structure solved using three-dimensional Patterson function, followed by successive Fourier syntheses. $S = 4{\cdot}84$. Max. $\Delta/\sigma = 0{\cdot}02$ (scale factor). Residual electron density peaks $< 3{\cdot}1$ e Å^{-3}. Atomic scattering factors and f' and f'' values from *International Tables for*

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X-ray Crystallography (1974); *Enraf–Nonius Structure Determination Package* (Frenz, 1980). Computer: PDP11-70.

Discussion. Table 1* reports the final coordinates and B_{eq}. Fig. 1 gives a projection of the atomic framework along the *b* axis. The coordinations of Ba and Bi atoms are indicated using dotted lines. Two independent units of PO_4 tetrahedra are distributed in the cell surrounding Ba and Bi atoms. The average ⟨P(1)—O⟩ and ⟨P(2)—O⟩ distances, 1·545 and 1·538 Å, are in good agreement with the mean ⟨P—O⟩ distances in many monophosphates (Liebau, 1970; Corbridge, 1974). One barium atom [Ba(1)] has an eightfold coordination, Ba(1)—O distances ranging from 2·803 to 2·891 Å. The other barium atom [Ba(2)] in special position 2(*e*) gives binary symmetry to the eight oxygen atoms surrounding it. The Bi atom has seven neighbours, from 2·274 to 2·847 Å. Table 2 shows all the interatomic distances for BiO_7 and BaO_8 polyhedra and PO_4 tetrahedra. The Bi—O_7 coordination is very distorted. If we compare the BiO_7 polyhedron to the BiO_8 dodecahedron in the high-temperature form of $BiPO_4$ (Masse & Durif, 1985), we find the same range of Bi—O distances: 2·15 to 2·90 Å. The BiO_8 arrangement is more regular. In $Bi_4(GeO_4)_3$ (Durif & Averbuch-Pouchot, 1982), the Bi coordination is octahedral with three Bi—O distances of 2·16 Å and three of 2·60 Å. The lone-pair effect is more marked than in the other type of Bi coordination. This type of coordination is rare. In oxides, the pyramidal BiO_5 coordination is frequent (Wells, 1984), as are the BiO_7 and the BiO_8.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42451 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates for* $Ba_3Bi_2(PO_4)_4$

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}(Å^2)
Bi	0·08095 (1)	0·44536 (4)	0·18808 (4)	0·700 (3)
Ba(1)	0·21676 (2)	0·06266 (6)	0·27532 (6)	0·671 (5)
Ba(2)	0	0·94447 (9)	$\frac{1}{4}$	0·604 (7)
P(1)	0·3888 (1)	0·7111 (3)	0·0090 (3)	0·56 (3)
P(2)	0·3553 (1)	0·1930 (3)	0·0499 (3)	0·56 (3)
O(1)	0·3091 (4)	0·7065 (10)	0·9233 (10)	1·2 (1)
O(2)	0·0787 (4)	0·6291 (9)	0·0024 (10)	1·3 (1)
O(3)	0·4263 (4)	0·4146 (9)	0·4513 (9)	1·2 (1)
O(4)	0·4046 (4)	0·3050 (8)	0·6959 (8)	0·88 (8)
O(5)	0·3304 (3)	0·0692 (8)	0·1471 (8)	0·95 (9)
O(6)	0·1706 (3)	0·3567 (8)	0·1327 (7)	0·68 (8)
O(7)	0·3277 (5)	0·3497 (9)	0·0613 (9)	1·5 (1)
O(8)	0·4351 (4)	0·1803 (10)	0·1037 (10)	1·3 (1)

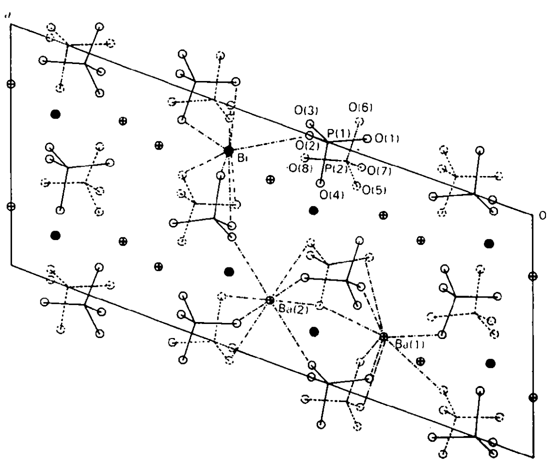

Fig. 1. Projection of $Ba_3Bi_2(PO_4)_4$ along the *b* axis.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the* PO_4 *tetrahedra and distances* (Å) *in the associated cation polyhedra, in* $Ba_3Bi_2(PO_4)_4$

P(1) tetrahedron				
P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1·535 (4)	2·581 (5)	2·537 (5)	2·513 (5)
O(2)	112·9 (2)	1·561 (4)	2·533 (5)	2·429 (5)
O(3)	112·5 (2)	110·8 (2)	1·517 (3)	2·520 (5)
O(4)	108·3 (2)	101·9 (2)	109·7 (2)	1·565 (3)

P(2) tetrahedron				
P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	1·563 (3)	2·530 (4)	2·557 (5)	2·481 (5)
O(6)	107·9 (2)	1·566 (3)	2·487 (5)	2·441 (5)
O(7)	113·4 (2)	108·6 (2)	1·495 (4)	2·555 (5)
O(8)	106·7 (2)	104·2 (2)	115·3 (2)	1·529 (3)

Ba(1) coordination			
Ba(1)—O(1)	2·864 (4)	Ba(1)—O(6)	2·869 (3)
Ba(1)—O(1)	2·756 (4)	Ba(1)—O(6)	2·803 (3)
Ba(1)—O(4)	2·809 (3)	Ba(1)—O(7)	2·879 (4)
Ba(1)—O(5)	2·891 (3)	Ba(1)—O(7)	2·684 (4)

Ba(2) coordination			
Ba(2)—O(3)	2·688 (3) (×2)	Ba(2)—O(4)	2·851 (3) (×2)
Ba(2)—O(3)	2·816 (4) (×2)	Ba(2)—O(8)	2·747 (4) (×2)

Bi coordination			
Bi—O(2)	2·274 (4)	Bi—O(5)	2·172 (3)
Bi—O(2)	2·847 (4)	Bi—O(6)	2·179 (3)
Bi—O(4)	2·387 (3)	Bi—O(8)	2·698 (4)
Bi—O(2)	3·164 (4)	Bi—O(8)	2·838 (4)

References

Corbridge, D. E. C. (1974). *The Structural Chemistry of Phosphorus*. Amsterdam, London, New York: Elsevier Scientific.

Durif, A. & Averbuch-Pouchot, M. T. (1982). *C.R. Acad. Sci. Sér. B*, **295**, 555–556.

Frenz, B. A. (1980). *Enraf–Nonius Structure Determination Package*. Version 17.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Liebau, F. (1970). *Phosphorus*. 15A. In *Handbook of Geochemistry* II. Berlin, Heidelberg, New York: Springer.

Masse, R. & Durif, A. (1985). *C.R. Acad. Sci. Sér. B*, **300**, 849–851.

Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., pp. 894–895. Oxford: Oxford Science Publications.