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Crystal data and crystal structure of bismuth tetraphosphate: $Bi_2P_4O_{13}$

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Abstract. Crystal chemistry and crystal structure are described for bismuth tetraphosphate $Bi_2P_4O_{13}$. The space group is monoclinic $C2/c$ with the unit cell parameters: $a = 11.977(4)$, $b = 6.878(2)$, $c = 13.285(4)$, $\beta = 106.50(2)$, $V = 1049(1)$ Å^3 and $Z = 4$. The structure has been solved using 1614 independent data with a final R value of 0.050. The P_4O_{13} anion has a twofold symmetry, the Bi atom located in the glide plane "c" is eightfold coordinated. The main characteristic of this atomic arrangement is a stacking of bidimensionally linked BiO_8 layers parallel to (001) planes connected together by P_4O_{13} groups lying in (010) planes.

Introduction

Among oligophosphates, the tetraphosphates are rather rare. Owing to the difficulty of producing monocrystals of these compounds, very few have been determined. Up to now only three crystal structures of tetraphosphates are well known: $(NH_4)_2SiP_4O_{13}$ (Durif, et al. 1976), $CaNb_2O(P_2O_7)(P_4O_{13})$ (Averbuch-Pouchot, in press) and $Pb_3P_4O_{13}$ (Averbuch-Pouchot and Durif, 1987).

Among the other reported tetraphosphates the bismuth salt $Bi_2P_4O_{13}$ is the most often mentioned in the literature: the first time by Schulz (1956), later on by Chudinova et al. (1972) and Tezikova et al. (1974). In these various articles only chemical preparation and non-indexed powder diagrams are given.

The present work reports accurate crystal data and the crystal structure of this salt confirming the anion is really a P_4O_{13} group as proposed in the previous studies.

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

Apparatus:	Philips PW 1100	Scan width: 1.20°
Wavelength:	Ag$K\bar{\alpha}$ (0.5608 Å)	Scan speed: 0.02° s^{-1}
Monochromator:	Graphite plate	Multiple scans for weak reflections
Scan mode:	ω	Number of collected reflections 1837 ($\pm HKL$)
Theta range:	3–30°	
Crystal size:	$0.12 \times 0.16 \times 0.24$ mm^3	$H_{max} = 23$, $K_{max} = 14$, $L_{max} = 23$
μ:	186 cm^{-1}	
$F(000)$; Mw:	1320; 749.85 a.m.v.	Total background measuring time: 20 s
		Reference reflections: $73\bar{6}$ and $\bar{7}\bar{3}6$

Crystal data

Single crystals of suitable size for X-ray diffraction studies were prepared by introducing 1.5 g K_2CO_3 and 1 g Bi_2O_3 into 5 cm^3 of H_3PO_4. This mixture was heated at 473 K for several hours, then kept at 513 K for 2 days. After removing the excess of flux by hot water, prismatic crystals were obtained and air dried.

Schulz (1956) reported that $Bi_2P_4O_{13}$ melts congruently at 1083 K. Later Hilmer et al. (1978) confirmed this temperature.

A preliminary single crystal study shows the symmetry to be monoclinic and the space group Cc or $C2/c$ (hkl with $h + k = 2n$, $h0l$ with $h = 2n$, $l = 2n$).

A least-squares refinement leads to the following unit cell constants: $a = 11.977(4)$, $b = 6.878(2)$, $c = 13.285(4)$ Å, $\beta = 106.50(2)°$, $V = 1049(1)$ $Å^3$, $Z = 4$, $D_x = 4.748$ Mg/m^3. An indexed powder diagram has been deposited[1].

Crystal structure determination

Experimental details about the intensity data collection parameters and various physical data are listed in Table 1. The lattice parameters were obtained by least-squares refinement from the angular settings of 20 reflections $10 < \theta < 14°$. They are in agreement with those reported above: $a = 12.009(10)$, $b = 6.885(5)$, $c = 13.306(12)$ Å, $\beta = 106.48(5)°$. Corrections for Lorentz and polarization effects and for absorption were applied (max. transmission = 17.80, min. = 10.93). The structure was solved using the centrosymmetric space group $C2/c$. Classical methods of crystal structure determination were employed: three-dimensional Patterson synthesis for locating Bi atoms and successive Fourier syntheses

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[1] Additional material to this paper can be ordered referring to the no. CSD 52558, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

for locating P and O atoms. After anisotropic full-matrix least-squares refinements on F the R value converged to 0.050 for 1614 reflections such that $|F_o - F_c| < 120$ in a scale $0-2854$. All the calculations were carried out with the Enraf-Nonius (1977) SDP programs. Scattering factors for neutral atoms and f', f'' were taken from International Tables for X-ray Crystallography (1974). A unitary weighting scheme was chosen all along the structure determination.

Table 2 reports the final atomic coordinates and B_{eq}. A list of anisotropic thermal coefficients has been deposited.

Description of the structure

Table 3 gives the main interatomic distances and bond angles in the P_4O_{13} anion and in the Bi environment.

Figure 1 represents the whole atomic arrangement down the $\vec{b}$ axis.

1. The tetraphosphate anion

Each P_4O_{13} group has a twofold symmetry around the central O(L22) oxygen atom. The P–O average distances are 1.540 Å and the O–P–O average angles are 109.4° for the two independent tetrahedra of the group. These average values are comparable to those observed in all condensed phosphate anions. The detailed geometrical features of the outer tetrahedron $P(1)O_4$ and of the inner tetrahedron $P(2)O_4$ are quite similar to those found in oligophosphates and in cyclo or long-chain phosphates.

In the unit cell the anionic groups run along the $\vec{a}$ axis near the glide plane "c". So they form layers perpendicular to $\vec{b}$ at $y = 0, 1/2$.

2. The environment of bismuth

The bismuth atom located on the glide plane "c" is surrounded by eight terminal oxygen atoms with Bi–O distances spreading from 2.179 to 2.799 Å. The BiO_8 polyhedron can be described as a distorted dodecahedron. This type of eightfold coordination is usual in Bi compounds. But the degree of distortion of the dodecahedral geometry can vary according to the type of linkage between the polyhedra: most of them are isolated as in $BiH(PO_3)_4$ (Palkina and Jost, 1975) or form chains as in $BiHNH_4P_3O_{10}$ (Averbuch-Pouchot and Bagieu-Beucher, in press). In $Bi_2P_4O_{13}$ the linkage between the BiO_8 groups is bidimensional along the $\vec{a}$ and $\vec{b}$ axes. A projection of such a layer down the $\vec{c}$ axis is given in Figure 2.

Each BiO_8 dodecahedron is linked to its neighbours by sharing common edges: O(E22)–O(E22)′ along $\vec{a}$, O(E12)–O(E12)′ and O(E13)–O(E13)′ along $\vec{b}$. The shortest Bi–Bi distance is 4.16 Å (4.08 Å in the unidimensional chains of $BiHNH_4P_3O_{10}$).

Table 2. Atomic coordinates and B_{eq} (Å^2) for $Bi_2P_4O_{13}$. Standard deviations in parentheses $B_{eq} = 4/3\ \Sigma_i \Sigma_j\ \vec{a}_i \vec{a}_j\ \beta_{ij}$.

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq}(\sigma)$
Bi	0.30323(3)	0.0004(1)	0.43853(2)	1.066(5)
P(1)	0.2305(2)	−0.0047(7)	0.1594(2)	0.99(3)
P(2)	0.4898(3)	0.3581(5)	0.1372(2)	1.12(4)
O(E11)	0.2003(8)	0.493(2)	0.2261(5)	1.7(1)
O(E12)	0.7537(8)	0.320(1)	0.0979(6)	1.4(1)
O(E13)	0.2499(8)	0.173(2)	0.0983(6)	1.5(2)
O(L12)	0.0959(7)	−0.002(2)	0.1531(6)	1.5(1)
O(E21)	0.6135(7)	0.493(2)	0.3940(6)	1.5(1)
O(E22)	0.5033(8)	0.194(1)	0.4339(7)	1.4(1)
O(L22)	1/2	0.269(2)	1/4	1.4(2)

Table 3. Main interatomic distances (Å) and bond angles (°) in the P_4O_{13} anion and the BiO_8 polyhedron. Standard deviations in parentheses.

P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.514(4)	113.6(4)	114.9(4)	108.2(2)
O(E12)	2.547(7)	1.529(6)	105.7(2)	108.5(4)
O(E13)	2.560(7)	2.432(7)	1.523(6)	105.7(3)
O(L12)	2.518(7)	2.534(8)	2.484(7)	1.594(5)
P(2)	O(E21)	O(L12)	O(L22)	O(E22)
O(E21)	1.512(6)	103.5(3)	109.6(2)	118.7(3)
O(L12)	2.414(6)	1.562(6)	105.6(2)	111.3(3)
O(L22)	2.538(7)	2.515(7)	1.594(3)	107.5(3)
O(E22)	2.583(9)	2.521(8)	2.489(5)	1.491(5)
P(1)−P(2)	2.974(2)	P(1)−O(L12)−P(2)		140.9(5)
P(2)−P(2)	2.941(3)	P(2)−O(L22)−P(2)		134.4(5)
	P(1)−P(2)−P(2)	95.8(1)		

Bi−O(E11)	2.179(4)
Bi−O(E12)	2.313(6)
Bi−O(E12)	2.665(5)
Bi−O(E12)	2.670(5)
Bi−O(E13)	2.356(6)
Bi−O(E21)	2.186(5)
Bi−O(E22)	2.764(5)
Bi−O(E22)	2.799(5)

Bi−Bi	4.161(1)	Bi−P(1)	3.296(1)	Bi−P(2)	3.514(2)

In conclusion, the structure consists of BiO_8 layers parallel to (001) planes at $z \approx 0,1/2$, connected together along the $\vec{c}$ axis by P_4O_{13} anionic groups lying in (010) planes. This structural arrangement explains the systematic weakness of reflections (hkl) with $l = 2n + 1$.

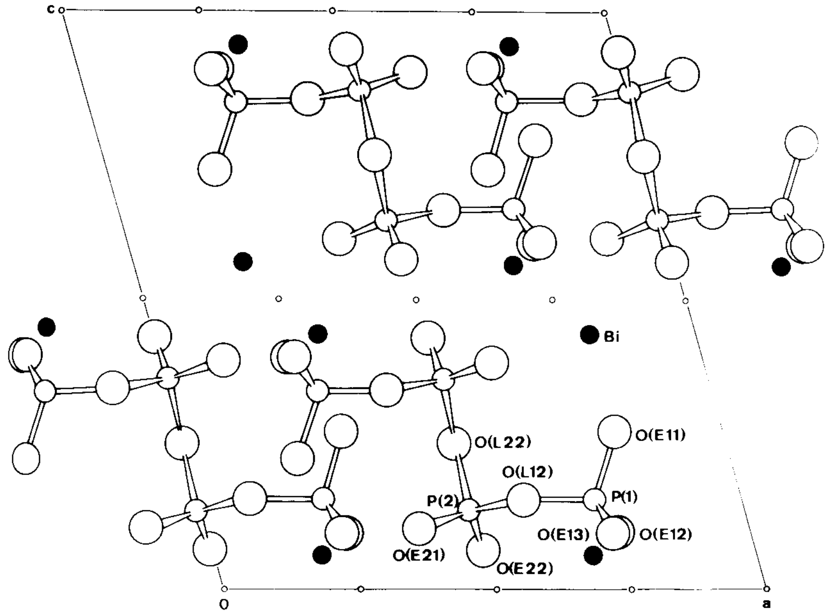

Fig. 1. Projection of the atomic arrangement of $Bi_2P_4O_{13}$ down the $\vec{b}$ axis.

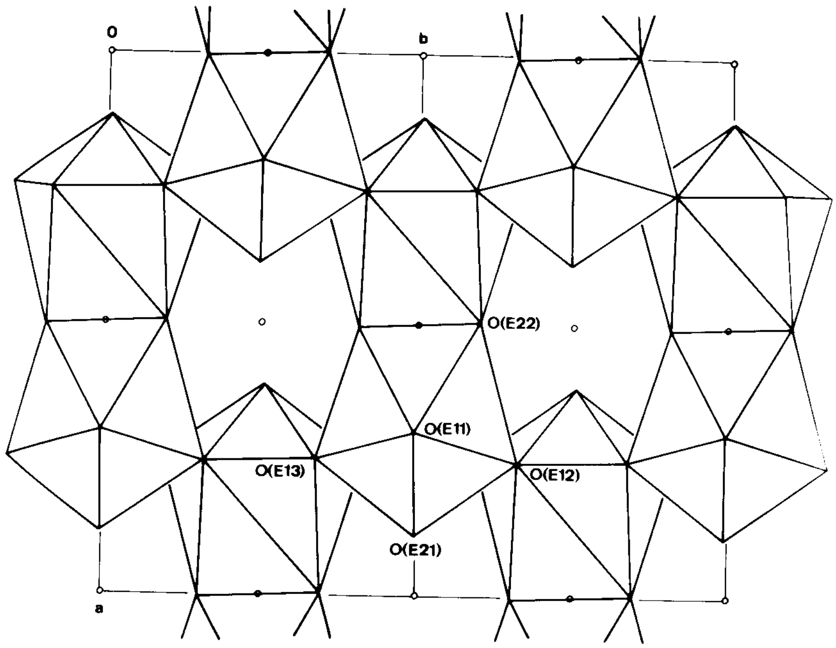

Fig. 2. Detailed projection of bidimensional BiO_8 linkages down $\vec{c}$.

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