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## Structure of Lead Tetrapolyphosphate

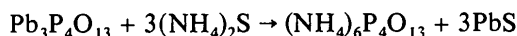
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**Abstract.**  $\text{Pb}_3\text{P}_4\text{O}_{13}$ ,  $M_r = 953.45$ , triclinic,  $P\bar{1}$ ,  $a = 7.830$  (5),  $b = 7.347$  (5),  $c = 10.215$  (8) Å,  $\alpha = 104.35$  (1),  $\beta = 101.81$  (1),  $\gamma = 94.27$  (1)°,  $V = 552.4$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 5.731$  Mg m<sup>-3</sup>,  $\lambda(\text{Ag K}\alpha) = 0.5608$  Å,  $\mu = 25.70$  mm<sup>-1</sup>,  $F(000) = 820$ ,  $T = 293$  K, final  $R = 0.048$  for 2634 independent observed reflexions. The phosphoric condensed anion is here a non-common tetrameric linear one,  $\text{P}_4\text{O}_{13}^{6-}$ , built up by four corner-sharing  $\text{PO}_4$  tetrahedra. The three independent Pb atoms, with a seven- or eightfold oxygen coordination, link these  $\text{P}_4\text{O}_{13}$  groups so as to build a three-dimensional network.

**Introduction.** Due to the lack of a general method of preparation, tetrapolyphosphates are rare and difficult to crystallize. Up to now only two crystal structures of tetrapolyphosphates have been performed:  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  (Durif, Averbuch-Pouchot & Guitel, 1976) and  $\text{CaNb}_2\text{O}(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$  (Averbuch-Pouchot, 1986). In this field of chemistry the title compound is an important starting material, since it has often been used during attempts to produce alkali tetrapolyphosphates by a metathesis reaction of the type:



(Waerstad & McClellan, 1974). The present work devoted to the crystal structure of  $\text{Pb}_3\text{P}_4\text{O}_{13}$  provides the third detailed geometrical configuration of a  $\text{P}_4\text{O}_{13}$  group.

**Experimental.** Crystal preparation and data have already been reported (Averbuch-Pouchot & Durif, 1986). Density not measured.  $0.19 \times 0.14 \times 0.29$  mm fragment of crystal. Philips PW 1100 diffractometer, graphite monochromator. 18 reflexions ( $10 < \theta < 12^\circ$ ) for refining unit-cell dimensions.  $\omega$  scan. 5032 reflexions measured ( $3 < \theta < 30^\circ$ ),  $\pm h \pm kl$ ,  $h_{\text{max}} = 13$ ,  $k_{\text{max}} = 12$ ,  $l_{\text{max}} = 17$ . Scan width  $1.20^\circ$ , scan speed

$0.02^\circ \text{ s}^{-1}$ , total background measuring time 20 s. Two intensity and orientation reference reflexions (120 and  $\bar{1}\bar{2}0$ ) every 2 h, no variation. Lorentz–polarization correction, absorption correction (max. = 40.5, min. = 20.4). Classical methods for structure determination: Patterson and successive Fourier syntheses. Anisotropic full-matrix least-squares refinement (on  $F$ ). Unit weights. Final refinement with 2634 reflexions such that  $I > 16\sigma_I$  and  $|F_o - F_c| < 20$  in a scale varying from 3468 to 0. Final  $R = 0.048$  ( $wR = 0.060$ ). For the complete set of 5032 reflexions  $R = 0.065$ .  $S = 5.536$ . Max.  $\Delta/\sigma = 0.02$  (for extinction coefficient). Max. peak height in final difference Fourier synthesis  $9.41 \text{ e } \text{Å}^{-3}$ . Extinction coefficient refined:  $0.37 \times 10^{-7}$  (Stout & Jensen, 1968). Scattering factors for neutral atoms and  $f'$ ,  $f''$  from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Final atomic coordinates and  $B_{\text{eq}}$  are reported in Table 1.\* Computer used: Digital PDP 11.70.

**Discussion.** The atomic arrangement of  $\text{Pb}_3\text{P}_4\text{O}_{13}$  projected along the  $b$  axis is shown in Fig. 1. The main interest of this structure rests on the presence of a tetrapolyphosphate anion  $\text{P}_4\text{O}_{13}^{6-}$ .

### The $\text{P}_4\text{O}_{13}$ group

As already mentioned this anion is a linear linkage of four corner-sharing  $\text{PO}_4$  tetrahedra. Table 2 reports the main geometrical features of this anion, built up by four crystallographically independent  $\text{PO}_4$  tetrahedra. A detailed comparison with previous examples of such

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43628 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

groups is difficult since only two of them have already been investigated, and in addition one of them, observed in  $\text{CaNb}_2\text{O}(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$ , has a twofold symmetry around the central bonding O atom. Nevertheless one can notice that the geometry of this  $\text{P}_4\text{O}_{13}$  group is close to that observed in long-chain polyphosphates for the two internal tetrahedra and similar to that observed in dipoly- or tripolyanions for the terminal tetrahedra.

The average P—O bond length observed in the title compound, 1.541 Å, is quite comparable to that observed in  $(\text{NH}_4)_2\text{SiP}_4\text{O}_{13}$  (1.539 Å) while the same average in the  $\text{P}_4\text{O}_{13}$  group of  $\text{CaNb}_2\text{O}(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$  is relatively shorter (1.526 Å) probably because of strains due to the internal symmetry of this group: a twofold axis around the central bonding oxygen.

Table 1. Atomic coordinates and  $B_{eq}$

$B_{eq} = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$ . Standard deviations are in parentheses.

	x	y	z	$B_{eq}(\text{Å}^2)$
Pb(1)	0.48156 (9)	0.2464 (1)	0.23124 (7)	1.347 (7)
Pb(2)	0.27124 (9)	0.3042 (1)	0.85226 (7)	1.327 (7)
Pb(3)	0.27198 (9)	0.7926 (1)	0.38156 (7)	1.384 (7)
P(1)	0.3036 (6)	0.3312 (6)	0.5099 (5)	0.99 (4)
P(2)	0.0343 (6)	0.8614 (7)	0.6613 (5)	1.13 (4)
P(3)	0.0410 (6)	0.3614 (7)	0.1388 (5)	1.09 (4)
P(4)	0.3039 (6)	0.8146 (7)	0.0295 (5)	1.11 (4)
O(E11)	0.647 (2)	0.576 (2)	0.335 (1)	1.7 (2)
O(E12)	0.613 (2)	0.848 (2)	0.530 (1)	1.6 (1)
O(E13)	0.322 (2)	0.466 (2)	0.421 (1)	1.2 (1)
O(L12)	0.904 (2)	0.741 (3)	0.524 (1)	1.9 (2)
O(E21)	-0.007 (2)	0.936 (2)	0.313 (2)	1.5 (1)
O(E22)	0.785 (2)	0.184 (3)	0.344 (3)	2.4 (2)
O(L23)	0.038 (2)	0.200 (2)	0.219 (1)	1.5 (1)
O(E31)	0.984 (2)	0.539 (2)	0.215 (2)	1.5 (1)
O(E32)	0.216 (2)	0.380 (2)	0.107 (1)	1.5 (1)
O(L34)	0.901 (2)	0.276 (2)	-0.003 (1)	1.2 (1)
O(E41)	0.308 (2)	-0.006 (2)	-0.018 (2)	2.2 (2)
O(E42)	0.378 (2)	0.854 (3)	0.185 (1)	2.0 (2)
O(E43)	0.613 (2)	0.348 (2)	0.051 (1)	1.6 (2)

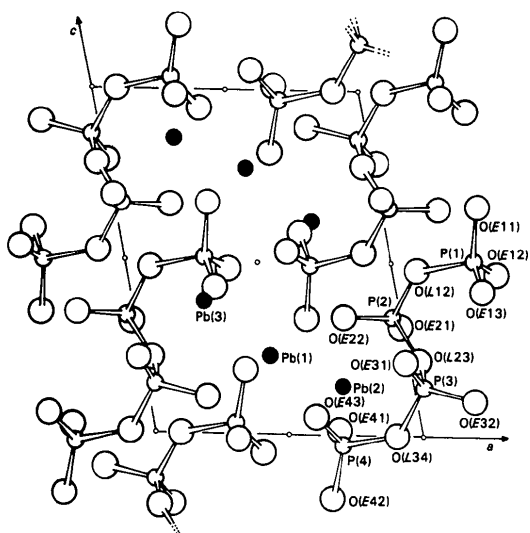


Fig. 1. Projection of the atomic arrangement of  $\text{Pb}_3\text{P}_4\text{O}_{13}$  along the  $b$  axis.

Table 2. Main interatomic distances (Å) and bond angles ( $^\circ$ ) in the atomic arrangement of  $\text{Pb}_3\text{P}_4\text{O}_{13}$

P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.520 (6)	112.4 (4)	114.7 (4)	104.6 (4)
O(E12)	2.521 (9)	1.515 (7)	113.9 (4)	104.5 (4)
O(E13)	2.559 (8)	2.544 (9)	1.520 (6)	105.4 (3)
O(L12)	2.478 (8)	2.472 (10)	2.491 (8)	1.610 (6)
P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	1.483 (6)	117.3 (4)	110.0 (4)	102.6 (4)
O(E22)	2.536 (10)	1.486 (7)	108.4 (4)	113.8 (4)
O(L12)	2.498 (10)	2.476 (8)	1.566 (6)	104.0 (3)
O(L23)	2.398 (9)	2.576 (9)	2.486 (9)	1.589 (7)
P(3)	O(E31)	O(E32)	O(L23)	O(L34)
O(E31)	1.496 (7)	116.4 (4)	111.9 (4)	108.3 (3)
O(E32)	2.528 (9)	1.478 (6)	107.1 (4)	107.6 (3)
O(L23)	2.570 (9)	2.480 (9)	1.605 (7)	104.8 (3)
O(L34)	2.493 (8)	2.468 (8)	2.523 (8)	1.578 (6)
P(4)	O(E41)	O(E42)	O(E43)	O(L34)
O(E41)	1.515 (8)	112.1 (4)	115.7 (4)	108.7 (4)
O(E42)	2.515 (12)	1.517 (7)	110.6 (4)	105.2 (3)
O(E43)	2.589 (10)	2.517 (9)	1.544 (7)	103.6 (3)
O(L34)	2.561 (9)	2.505 (8)	2.499 (10)	1.635 (6)
P(1)—P(2)	2.895 (3)	P(1)—O(L12)—P(2)	131.3 (4)	
P(2)—P(3)	3.034 (3)	P(2)—O(L23)—P(3)	143.6 (4)	
P(3)—P(4)	2.898 (3)	P(3)—O(L34)—P(4)	128.7 (4)	
Pb(1)—O(E11)	2.525 (6)	Pb(2)—O(E11)	2.464 (7)	
Pb(1)—O(E12)	2.911 (7)	Pb(2)—O(E21)	2.609 (6)	
Pb(1)—O(E13)	2.765 (7)	Pb(2)—O(E31)	2.442 (6)	
Pb(1)—O(E22)	2.548 (7)	Pb(2)—O(E32)	2.654 (6)	
Pb(1)—O(E32)	2.594 (6)	Pb(2)—O(E41)	2.910 (8)	
Pb(1)—O(E41)	2.766 (7)	Pb(2)—O(E43)	2.950 (6)	
Pb(1)—O(E42)	2.830 (8)	Pb(2)—O(E43)	2.524 (7)	
Pb(1)—O(E43)	2.515 (7)			
Pb(3)—O(E12)	2.732 (6)			
Pb(3)—O(E12)	2.596 (7)			
Pb(3)—O(E13)	2.574 (6)			
Pb(3)—O(E21)	2.541 (6)			
Pb(3)—O(E22)	2.891 (7)			
Pb(3)—O(E31)	2.770 (6)			
Pb(3)—O(E42)	2.452 (7)			

### The associated cations

Three crystallographically independent Pb atoms maintain the cohesion of the three-dimensional framework. Within a range of 3 Å, Pb(2) and Pb(3) have a sevenfold coordination while Pb(1) has eight neighbours.

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