

Crystal structure of lead-tetrasodium trimetaphosphate: $\text{PbNa}_4(\text{P}_3\text{O}_9)_2$, Crystal data for $\text{BaNa}_4(\text{P}_3\text{O}_9)_2$

M. T. Averbuch-Pouchot and A. Durif

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique,
Laboratoire associé à l'U.S.M.G., 166X, F-38042 Grenoble-Cédex, France

Received: February 21, 1983

Inorganic phosphates / Crystal structure / Inorganic ring anion

Abstract. Lead tetrasodium trimetaphosphate $\text{PbNa}_4(\text{P}_3\text{O}_9)_2$ is triclinic, $P\bar{1}$ with $a = 7.268(4)$, $b = 8.151(5)$, $c = 7.851(5)$ Å, $\alpha = 121.52(5)$, $\beta = 102.06(5)$, $\gamma = 73.00(5)^\circ$, $Z = 1$, $V = 378.3$ Å³ and $d_x = 3.393$ g/cm³. Its crystal structure has been solved using 1507 reflexions, with a final R value 0.049 for 1268 reflexions. The atomic arrangement is characterized by a disorder between Pb and Na on one crystallographic site. Chemical preparation and crystal data are given for the isotypic barium salt: $\text{BaNa}_4(\text{P}_3\text{O}_9)_2$.

Introduction

Lead tetrasodium trimetaphosphate: $\text{PbNa}_4(\text{P}_3\text{O}_9)_2$ has been characterized during the study of the $\text{Pb}(\text{PO}_3)_2$ - NaPO_3 equilibrium phase diagram (Mahama et al., 1975), and recognized as a trimetaphosphate by chromatographic analysis.

Barium tetrasodium trimetaphosphate: $\text{BaNa}_4(\text{P}_3\text{O}_9)_2$ was also characterized when establishing the $\text{Ba}(\text{PO}_3)_2$ - NaPO_3 equilibrium phase diagram (Martin et al., 1972) but the relationship with the lead salt has never been investigated from a crystallographic point of view. Both are congruent melting compounds with melting points of 913 K and 939 K respectively. The present study shows the isotypism of these two salts and gives the crystal structure of this class of compounds.

Crystal data

Single crystals of the lead compound have been prepared according to the procedure described by Mahama et al. (1975). Single crystals of the barium salt were prepared by introducing 0.75 g of barium carbonate and 2 g of sodium carbonate into 6 cm³ of monophosphoric acid (85%). This mixture was then

Table 3. Final atomic coordinates for $\text{PbNa}_4(\text{P}_3\text{O}_9)_2 \cdot B_{\text{eq}}$ are calculated from $B_{\text{eq}} = 4/3 E_{\text{eq}}^2 / \beta_j a_j$. Estimated standard deviations are given in parentheses

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{\text{eq}}(\sigma)$
{0.5Pb + 0.5Na(1)}	0.0797(1)	0.1970(1)	0.16961(9)	1.84(1)
P(1)	0.2307(3)	0.9791(3)	0.6795(3)	0.98(3)
P(2)	0.5046(3)	0.7785(3)	0.0464(3)	0.89(3)
P(3)	0.7656(3)	0.6671(3)	0.3209(3)	0.87(3)
Na(2)	0.1788(5)	0.6575(5)	0.1759(5)	1.74(6)
Na(3)	0.5000(0)	0.5000(0)	0.5000(0)	1.39(8)
O(E11)	0.2525(9)	0.7702(8)	0.5205(9)	1.50(10)
O(E12)	0.0739(9)	0.0708(8)	-0.1789(8)	1.44(10)
O(L12)	0.4332(9)	0.0115(7)	0.8058(8)	1.16(10)
O(L13)	0.2062(9)	0.1102(7)	0.5745(8)	1.09(10)
O(E21)	0.2919(9)	0.8213(8)	0.0189(8)	1.55(10)
O(E22)	0.3732(10)	0.3420(8)	0.1289(8)	1.63(12)
O(E31)	0.2630(10)	0.3652(8)	0.5188(8)	1.57(12)
O(E32)	0.0780(9)	0.4719(8)	-0.1827(8)	1.43(11)
O(L23)	0.4368(9)	0.3192(7)	0.8094(7)	1.09(10)

Table 4. Main interatomic distances (Å) and bond angles (°) in the P_3O_9 ring anion. Standard deviations in parentheses

P(1)O ₄ Tetrahedron					
P(1)	O(E11)	O(E12)	O(L12)	O(L13)	
O(E11)	1.478(4)	2.575(6)	2.507(6)	2.502(6)	
O(E12)	119.6(3)	1.502(5)	2.529(6)	2.527(6)	
O(L12)	109.0(2)	109.2(3)	1.600(5)	2.483(6)	
O(L13)	108.0(3)	108.4(2)	101.2(2)	1.613(4)	
P(2)O ₄ Tetrahedron					
P(2)	O(E21)	O(E22)	O(L12)	O(L13)	
O(E21)	1.477(5)	2.591(7)	2.495(6)	2.490(6)	
O(E22)	121.3(3)	1.493(4)	2.552(6)	2.547(6)	
O(L12)	107.0(3)	109.7(3)	1.624(5)	2.501(6)	
O(L23)	106.7(3)	109.4(3)	100.7(2)	1.625(4)	
P(3)O ₄ Tetrahedron					
P(3)	O(E31)	O(E32)	O(L13)	O(L23)	
O(E31)	1.477(5)	2.561(7)	2.492(6)	2.521(6)	
O(E32)	119.1(3)	1.493(3)	2.540(6)	2.538(6)	
O(L13)	107.4(3)	109.7(3)	1.613(4)	2.491(6)	
O(L23)	109.0(3)	109.3(2)	100.9(2)	1.618(4)	
P(1)–P(2)	2.878(2)	P(1)–O(L12)–P(2)	126.4(3)	P(2)–P(1)–P(3)	60.29(5)
P(1)–P(3)	2.894(2)	P(1)–O(L13)–P(3)	127.5(3)	P(1)–P(2)–P(3)	60.13(5)
P(2)–P(3)	2.898(2)	P(2)–O(L23)–P(3)	126.7(3)	P(1)–P(3)–P(2)	59.58(5)

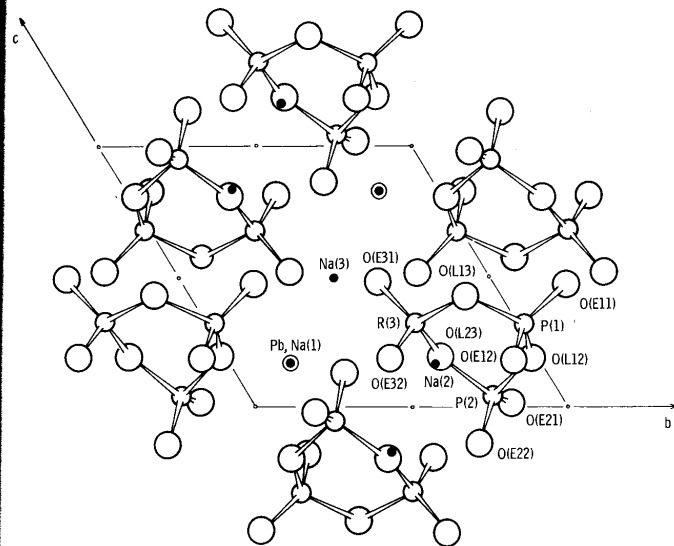


Fig. 1. Projection on (100) of $\text{PbNa}_4(\text{P}_3\text{O}_9)_2$.

criteria: $|F_0| > 2\sigma(F_0)$ and $|F_0 - F_c| < 55$ in a scale 0–1264. For the complete set of 1507 reflexions R is 0.062. Table 3 reports the final atomic coordinates¹.

Description of the structure

As shown in Figure 1 the atomic arrangement can be described as P_3O_9 rings setting in rows in (011) planes. The Na(2) atoms are located in the same planes and maintain the cohesion between P_3O_9 rings inside these planes, while the other cations, Na(3) and (Pb, Na) are located in (011) planes, alternating with the first ones, and maintain cohesion between P_3O_9 planes.

Table 4 reports the main interatomic distances and bond angles in the P_3O_9 ring anion. In spite of the lack of any symmetry element, this ring is quite regular: $59.58 < \text{P}–\text{P}–\text{P} < 60.29^\circ$ and $2.878 < \text{P}–\text{P} < 2.898 \text{ \AA}$, with average $\text{P}–\text{O}$ distances 1.548, 1.555 and 1.550 Å for the three tetrahedra.

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please state ref. no. CSD 50444, names of the authors and citation of the paper.

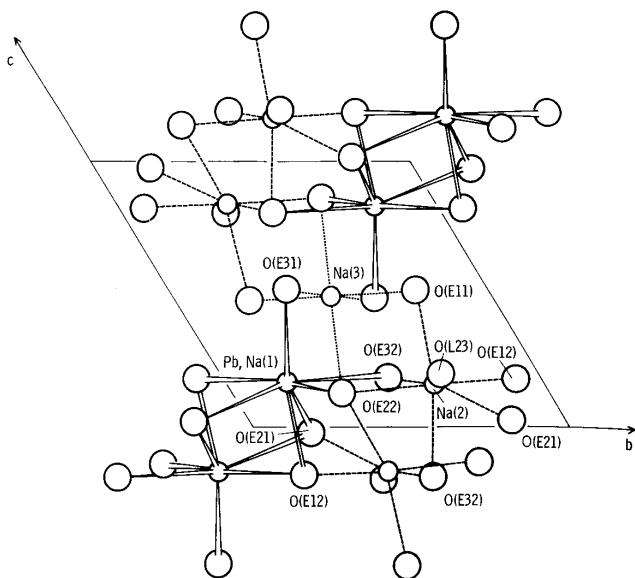


Fig. 2. Projection on (100) of the associated cation polyhedra. Phosphorus atoms are not represented

Table 5. Main interatomic distances (Å) in cation polyhedra. Standard deviations are in parentheses

[0.5. Pb, 0.5 Na(1)]O ₆ polyhedron			
M—O(E12)	2.362(5)	M—O(E22)	2.864(5)
M—O(E12)	2.764(5)	M—O(E31)	2.604(5)
M—O(E21)	2.714(5)	M—O(E32)	2.561(5)
M—O(E21)	2.800(5)		
Na(2)O ₇ polyhedron			
Na(2)		Na(2)	
—O(E11)	2.353(5)	—O(E32)	2.466(5)
Na(2)		Na(2)	
—O(E12)	2.421(5)	—O(E32)	2.419(6)
Na(2)		Na(2)	
—O(E21)	2.600(5)	—O(L23)	2.829(5)
Na(2)			
—O(E22)	2.418(5)		
Na(3)O ₆ polyhedron			
Na(3)—O(E11)	2.355(4) (× 2)		
Na(3)—O(E22)	2.578(5) (× 2)		
Na(3)—O(E31)	2.362(5) (× 2)		

The sodium atom Na(3), located on an inversion center, has a six-fold coordination with Na—O distances ranging from 2.355 to 2.578 Å. The sodium atom Na(2) has a seven-fold coordination with six close distances Na—O ranging from 2.353 to 2.600 Å and a seventh one of 2.829 Å, corresponding to a bond with an internal oxygen [O(L23)] of the ring. More interesting is the polyhedron corresponding to the mixed cation Pb—Na. Two of these polyhedra are located close to the origin with a very short cation-cation distance of 3.270 Å. These two centrosymmetric polyhedra share a rectangular face as shown in Figure 2. This kind of disorder is to be compared with the Ba—Na disorder observed in NaBaPO₄ (Kolsi et al., 1981).

A general view of the cation polyhedra arrangement is given in Figure 2, while Table 5 reports the main interatomic distances in these polyhedra.

References

- Kolsi, A. W., Querton, M., Freundlich, W.: Structure cristalline de NaBaPO₄. *J. Solid State Chem.* **36**, 107–111 (1981)
- Mahama, I., Averbuch-Pouchot, M. T., Grenier, J. C.: Etude du système NaPO₃—Pb(PO₃)₂. *C. R. Acad. Sci. Paris*, **280C**, 1105–1107 (1975)
- Martin, C., Durif, A.: Etude des systèmes NaPO₃—Ba(PO₃)₂ et NaPO₃—Sr(PO₃)₂. Données cristallographiques sur BaNa(PO₃)₃, SrNa(PO₃)₃·4H₂O et SrNa(PO₃)₃·3H₂O. *Bull. Soc. Fr. Minéral. Cristallogr.* **95**, 149–153 (1972)