

O(13)···O(22) = 2,53 Å; O(23)—H···O(12) avec O(23)···O(12) = 2,60 Å; P(2)—O(23)—O(12) = 103°; P(1)—O(13)—O(22) = 106°. Ce réseau de liaison hydrogène assure la rigidité du réseau.

Références

- JOHANSSON, G. B. & LINDQUIST, O. (1976). *Acta Cryst.* **B32**, 412–414.
- LARBOT, A., DURAND, J. & COT, L. (1984). *Z. Inorg. Allg. Chem.* **508**, 154–158.
- LOUB, J., PODLAHOVÁ, J. & JEČNÝ, J. (1978). *Acta Cryst.* **B34**, 32–34.
- LOUKILI, M., DURAND, J., COT, L. & RAFIQ, M. (1988). *Acta Cryst.* **C44**, 6–8.
- LOUKILI, M., DURAND, J., LARBOT, A., COT, L. & RAFIQ, M. (1991). *Acta Cryst.* **C47**, 477–479.
- PHILIPPOT, E. & LINDQUIST, O. (1970). *Acta Chem. Scand.* **24**, 2803–2810.
- SGHYAR, M., DURAND, J., COT, L. & RAFIQ, M. (1990). *Acta Cryst.* **C46**, 1378–1381.
- SGHYAR, M., DURAND, J., COT, L. & RAFIQ, M. (1991). *Acta Cryst.* **C47**, 8–10.
- SHELDRIK, G. M. (1976). *SHELX76*. Programme pour la détermination de structures cristallines. Univ. de Cambridge, Angleterre.
- SHELDRIK, G. M. (1986). *SHELXS86*. Programme pour la détermination de structures cristallines. Univ. de Göttingen, Allemagne.
- TIJANI, N., DURAND, J. & COT, L. (1988). *Acta Cryst.* **C44**, 2048–2050.

Acta Cryst. (1992). **C48**, 1173–1176

Structure of Nonasilver Sodium *cyclo*-Octaphosphate Dinitrate Tetrahydrate: Ag₉NaP₈O₂₄(NO₃)₂·4H₂O

BY MARIE-THÉRÈSE AVERBUCH-POUCHOT AND ANDRÉ DURIF

Laboratoire de Cristallographie, associé à l'Université J. Fourier, CNRS, BP 166,
38042 Grenoble CEDEX 09, France

(Received 3 October 1991; accepted 5 December 1991)

Abstract. Ag₉NaP₈O₂₄(NO₃)₂·4H₂O, $M_r = 1821.638$, orthorhombic, *Cmcm*, $a = 17.254$ (5), $b = 7.543$ (1), $c = 23.465$ (5) Å, $V = 3054$ (2) Å³, $Z = 4$, $D_x = 3.961$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0.5608$ Å, $\mu = 3.086$ mm⁻¹, $F(000) = 3392$, $T = 294$ K, final $R = 0.044$ for 1614 reflections. The title compound provides the first evidence for the coexistence of NO₃ groups and condensed phosphoric anions in an atomic arrangement. The P₈O₂₄ ring anion has 2/*m* internal symmetry, while the NO₃ group has mirror symmetry. Layers containing the phosphoric rings alternate with layers of NO₃ groups perpendicular to the *c* direction, while all the water molecules are located in planes $x = 0$ and $\frac{1}{2}$. A statistical Ag–Na distribution is observed for one of the cation positions. Two of the four water molecules are not involved in the associated cation polyhedra.

Introduction. More than 20 years ago Schülke (1968*a,b*) reported a process for the production of convenient amounts of sodium *cyclo*-octaphosphate hexahydrate, Na₈P₈O₂₄·6H₂O. In spite of the possibility offered to explore *cyclo*-octaphosphate chemistry by using this salt as a starting material, the rare examples of *cyclo*-octaphosphates investigated in detail since this date have been characterized either during elaborations of phase-equilibrium diagrams,

or during the investigation of various systems by flux methods. A series of four isotopic compounds Cu₃M₂P₈O₂₄ was characterized during the elaboration of the MPO₃–Cu₂P₄O₁₂ phase-equilibrium diagrams for $M = \text{Rb, Cs and Tl}$ (Laügt, Scory & Durif, 1968; Laügt & Martin, 1972; Laügt, 1974*a,b,c*) and for the ammonium salt during an investigation of the CuO–P₂O₅–(NH₄)₂O system (Laügt, 1974*c*; Laügt & Guitel, 1975). Other *cyclo*-octaphosphates of general formula M₂K₂P₈O₂₄ with $M = \text{Al, Fe}$ (Grunze, Chudinova & Palkina, 1983), $M = \text{Ga}$ (Palkina, Maksimova, Kusnetsov & Chudinova, 1979) and $M = \text{V}$ (Lavrov, Voitenkov & Tselebrovskaya, 1981), were discovered during investigations of the corresponding K₂O–P₂O₅–M₂O₃ systems by flux methods. In all cases, the true nature of the anion was recognized during the structural investigations. Recently, the atomic arrangement of Na₈P₈O₂₄·6H₂O was determined by Schülke, Averbuch-Pouchot & Durif (1992).

In order to generalize Boullé's metathesis reaction (Boullé, 1938) commonly used for the production of water-soluble *cyclo*-phosphates, we tried to prepare a silver *cyclo*-octaphosphate. During these attempts we identified various mixed compounds and among them Ag₉NaP₈O₂₄(NO₃)₂·4H₂O, the object of the present structural investigation. The formation of

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for Ag₉NaP₈O₂₄(NO₃)₂·4H₂O, with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B _{eq}
Ag(1)	0	0.3385 (1)	0.03390 (4)	1.74 (1)
Ag(2)	0.21658 (5)	0.3718 (1)	0.14692 (3)	2.50 (1)
Ag(3)	0.38723 (8)	0.2476 (2)	↓	2.92 (2)
Ag(4)	0.3160 (1)	0	0	4.63 (5)
Na(4)	0.3160	0	0	4.63
P(1)	0.1376 (1)	0.0385 (3)	0.43819 (8)	1.07 (3)
P(2)	0.4160 (1)	0.2084 (2)	0.38980 (7)	1.00 (2)
O(E11)	0.1192 (4)	0.2272 (8)	0.0765 (2)	2.0 (1)
O(L11)	0.1012 (4)	0	0	1.4 (1)
O(L12)	0.4166 (3)	0.4188 (7)	0.3990 (2)	1.27 (8)
O(E12)	0.2816 (3)	0.4734 (9)	0.0650 (2)	2.1 (1)
O(E21)	0.4128 (4)	0.1185 (8)	0.0533 (2)	1.66 (9)
O(E22)	0.3582 (4)	0.1593 (8)	0.1541 (2)	1.9 (1)
O(L22)	↓	0.1843 (9)	0.3612 (3)	1.2 (1)
N	0.1828 (6)	0.152 (1)	↓	1.7 (2)
O(1)	0.2096 (8)	0.305 (2)	↓	4.2 (2)
O(2)	0.1701 (5)	0.077 (1)	0.2043 (3)	3.6 (1)
O(W1)	0	0.239 (1)	0.1692 (4)	2.7 (2)
O(W2)	0	0.958 (2)	↓	3.0 (3)
O(W3)	0	0.522 (2)	↓	3.2 (3)

mixed phosphate–nitrates was observed several times during the preparation of the silver salts of higher ring phosphates. This fact is very probably to be attributed to the complexing ability increasing with the ring size in the alkali derivatives.

Experimental. Crystals of the title compound were obtained by adding a diluted aqueous solution of silver nitrate to an aqueous solution of Na₈P₈O₂₄·6H₂O in the stoichiometric ratio required to obtain Ag₈P₈O₂₄. After some days of digestion at room temperature, the amorphous precipitate transformed into large multifaceted polyhedra having a strong pseudo-ternary symmetry.

Crystal size 0.24 × 0.24 × 0.24 mm. Density not measured. Philips PW1100 diffractometer, graphite monochromator. 17 reflections (10.50 < θ < 12.10°) for refining unit-cell dimensions. ω scan, scan width 1.20°, scan speed 0.02° s⁻¹; total background-measuring time 6 s. 4983 scanned reflections (3 < θ < 30°), 2436 non-zero reflections; h, k, l: h_{max} = 28, k_{max} = 12, l_{max} = 41. Two orientation and intensity control reflections (10,0,8 and $\bar{1}0,0,\bar{8}$), measured every 4 h showed no significant variation. Lorentz and polarization corrections. Spherical absorption correction with transmission factors between 0.562 and 0.556.

Crystal structure solved using direct methods (MULTAN77; Main, Lessinger, Woolfson, Germain & Declercq, 1977) for the location of the heavy atoms and successive Fourier syntheses. H atoms not located. During the first preliminary refinements, it clearly appeared that the high temperature factor observed for one of the Ag-atom positions was to be attributed to the presence of both Ag and Na atoms on this site. Then, simultaneously with the estimation of the Ag/Na ratio by refinement of the occupancy

rates from the diffraction data, an analysis of the P/Ag ratio was run by energy dispersion spectrometry (EDS) on a Kevex Quantum/Jeol 840 A. Both methods converged towards the values calculated from the formula Ag₉NaP₈O₂₄(NO₃)₂·4H₂O: Ag/P = 1.128 found by EDS (calculated 1.125) and Ag/Na = 8.3 by X-ray refinement (calculated 9) but, as expected, with a larger experimental deviation. Anisotropic full-matrix least-squares refinement (on F); unit weights. Scattering factors for neutral atoms and f', f'' values from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf-Nonius (1977) SDP used for all calculations on a MicroVAX II computer. No secondary-extinction correction. Final refinements with 1614 reflections [$I > 4\sigma(I)$] gave $R = 0.044$ ($wR = 0.046$), $S = 3.749$, maximum $\Delta/\sigma = 0.0$, maximum peak height in the final difference Fourier synthesis = 0.66 e \AA^{-3} .

Table 1 reports the final atomic coordinates for this atomic arrangement.* Figs. 1 and 2 were prepared using STRUPLO84 (Fischer, 1985).

Discussion. The main interest in the present atomic arrangement lies in the geometrical characterization of a new P₈O₂₄ ring anion and in the coexistence in the same structure of NO₃ groups and condensed phosphoric entities. Some rare examples of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54944 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0262]

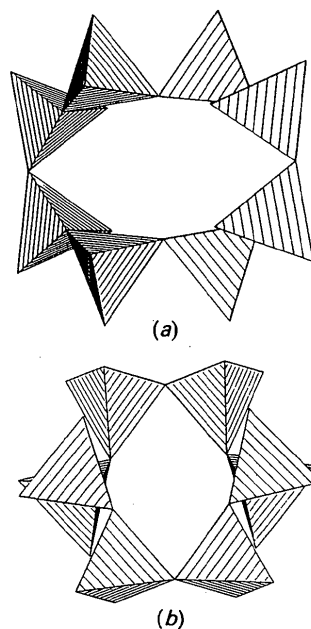


Fig. 1. Projection of the phosphoric ring anion along (a) the b direction and (b) the c direction.

phosphate–nitrates are known but, up to now, in all cases they are monophosphate nitrates.

The phosphoric ring anion. Main interatomic distances and bond angles in the two independent PO₄ tetrahedra building the phosphoric ring are given in Table 2. These values are to be compared with those corresponding to the only previously reported P₈O₂₄ ring having the same 2/m internal symmetry, observed in K₂Ga₂P₈O₂₄ (Grunze *et al.*, 1983). The P—O—P angles and the P—P distances are all in the ranges generally measured in condensed phosphoric anions, but the P—P—P angles show significant variations. The two P—P—P angles measured in K₂Ga₂P₈O₂₄ (131.4 and 138.0°) are much larger than those observed in the title compound (102.5 and 108.7°), showing that the present ring departs very strongly from the ideal planarity corresponding to a P—P—P angle of 135° for an eight-membered ring. The compact geometry of the present ring can be clearly seen in the two different projections of this anion given in Fig. 1. As shown by Fig. 2, reporting the whole atomic arrangement in projection along the *b* direction, all the P₈O₂₄ entities lie perpendicular to this direction forming arrays spreading around planes $z = 0$ and $\frac{1}{2}$.

The NO₃ group. The central N atom and one of the O atoms of this group are located in a mirror plane. The values of the O—N—O angles [121.0 and 119.3° ($\times 2$)] show this group to be almost planar within the range of the experimental errors. All these groups spread in planes $z = \frac{1}{4}$ and $\frac{3}{4}$ alternating with the layers of the phosphoric groups.

The Ag atoms. Within a range of 3 Å, three of the four Ag atoms have sixfold coordination polyhedra with various symmetries. Ag(1) and Ag(3) are located on mirror planes while Ag(4) is situated on a twofold axis. This last site is in fact partly filled by

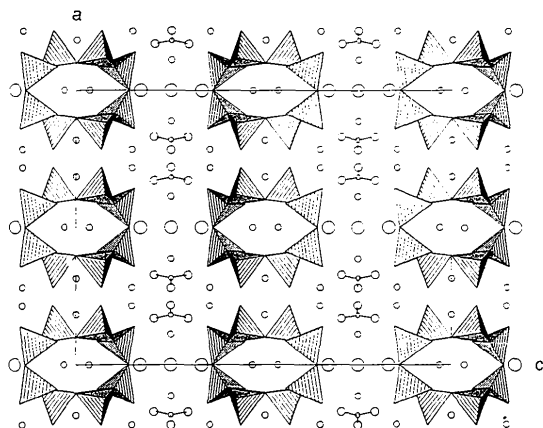


Fig. 2. Projection of the atomic arrangement of Ag₉NaP₈O₂₄(NO₃)₂.4H₂O along the *b* direction. By order of decreasing size empty circles represent water molecules, O atoms of the NO₃ groups, Ag atoms and N atoms.

Table 2. Main interatomic distances (Å) and bond angles (°) in the atomic arrangement of Ag₉NaP₈O₂₄(NO₃)₂.4H₂O, with *e.s.d.*'s in parentheses

P ₈ O ₂₄ ring anion					
P(1)O ₄ tetrahedron					
P(1)	O(E11)	O(L11)	O(L12)	O(E12)	
O(E11)	1.499 (6)	2.501 (6)	2.475 (8)	2.582 (9)	
O(L11)	107.2 (3)	1.607 (3)	2.468 (5)	2.541 (8)	
O(L12)	106.3 (3)	100.9 (3)	1.593 (5)	2.512 (8)	
O(E12)	120.2 (4)	110.7 (3)	109.6 (3)	1.479 (6)	
P(2)O ₄ tetrahedron					
P(2)	O(L12)	O(E21)	O(E22)	O(L22)	
O(L12)	1.601 (5)	2.527 (7)	2.529 (8)	2.447 (8)	
O(E21)	109.2 (3)	1.498 (5)	2.563 (7)	2.555 (8)	
O(E22)	110.2 (3)	118.8 (3)	1.480 (6)	2.480 (6)	
O(L22)	99.3 (3)	110.7 (3)	106.8 (3)	1.608 (3)	
P(1)—P(1)	2.958 (2)	P(1)—O(L11)—P(1)	133.9 (5)	P(1)—P(1)—P(2)	102.50 (7)
P(1)—P(2)	2.889 (3)	P(1)—O(L12)—P(2)	129.5 (3)	P(1)—P(2)—P(2)	108.68 (8)
P(2)—P(2)	2.900 (3)	P(2)—O(L22)—P(2)	128.8 (4)		
AgO _n and (Ag,Na)O ₆ polyhedra					
Ag(1)—O(E11)	2.436 (6) $\times 2$	Ag(4)—O(E11)	2.950 (6) $\times 2$		
Ag(1)—O(E21)	2.633 (6) $\times 2$	Ag(4)—O(E12)	2.281 (6) $\times 2$		
Ag(1)—O(E21)	2.561 (5) $\times 2$	Ag(4)—O(E21)	2.270 (6) $\times 2$		
Ag(2)—O(E11)	2.597 (6)	Ag(3)—O(E22)	2.401 (5) $\times 2$		
Ag(2)—O(E12)	2.354 (6)	Ag(3)—O(2)	2.883 (8) $\times 2$		
Ag(2)—O(E22)	2.528 (6)	Ag(3)—O(W2)	2.512 (10)		
Ag(2)—O(E22)	2.927 (6)	Ag(3)—O(W3)	2.584 (11)		
Ag(2)—O(1)	2.474 (2)				
Ag(2)—O(2)	2.719 (8)				
Ag(2)—O(2)	2.834 (8)				
NO ₃ group					
N—O(1)	1.24 (2)	O(2)—N—O(2)	121 (1)		
N—O(2)	1.231 (9) $\times 2$	O(1)—N—O(2)	119.3 (6) $\times 2$		

Na atoms (see *Experimental*). The last Ag atom Ag(2) is in general position and has seven neighbours within the same range of distances. It is notable that in the Ag(1)O₆, Ag(2)O₇ and Ag(3)O₆ polyhedra the Ag—O distances vary regularly between 2.354 and 2.927 Å, while in the Ag(Na)O₆ polyhedron one observes two pairs of short distances (2.270 and 2.281 Å) and a pair of significantly longer distances (2.950 Å).

Water molecules. The three independent water molecules are located on special positions, O(W1) in a mirror plane and the two remaining ones on sites with *mm* symmetry. All are located in planes $x = 0$ and $\frac{1}{2}$. In addition, it must be noted that O(W1) is not involved in the associated cation polyhedra and within a range of 3 Å has only two neighbours, O(W2) and O(W3), at respective distances of 2.842 and 2.855 Å, probably corresponding to the hydrogen bonds.

The authors wish to express their warm thanks to Dr T. Fournier for a very careful analysis of crystals by EDS and very instructive discussions on the possibilities of this method.

References

- BOULLÉ, A. (1938). *C. R. Acad. Sci.* **206**, 517–519.
 Enraf–Nonius (1977). *Structure Determination Package*. Version RSX-11M. Enraf–Nonius, Delft, The Netherlands.

- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
 GRUNZE, I., CHUDINOVA, N. N. & PALKINA, K. K. (1983). *Izv. Akad. Nauk SSSR Neorg. Mater.* **19**, 1943–1945.
 LAÜGT, M. (1974a). *C. R. Acad. Sci. Sér. C*, **278**, 1197–1200.
 LAÜGT, M. (1974b). *C. R. Acad. Sci. Sér. C*, **278**, 1497–1500.
 LAÜGT, M. (1974c). Thesis. Univ. of Grenoble, France.
 LAÜGT, M. & GUITEL, J. C. (1975). *Z. Kristallogr.* **141**, 203–216.
 LAÜGT, M. & MARTIN, C. (1972). *Mater. Res. Bull.* **7**, 1525–1534.
 LAÜGT, M., SCORY, M. & DURIF, A. (1968). *Mater. Res. Bull.* **3**, 963–970.
 LAVROV, A. V., VOITENKOV, M. YA. & TSELEBROVSKAYA, E. G. (1981). *Izv. Akad. Nauk SSSR Neorg. Mater.* **17**, 99–103.
 MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 PALKINA, K. K., MAKSIMOVA, S. I., KUSNETSOV, V. G. & CHUDINOVA, N. N. (1979). *Dokl. Akad. Nauk SSSR*, **245**, 1386–1389.
 SCHÜLKE, U. (1968a). *Angew. Chem. Int. Ed. Engl.* **7**, 71.
 SCHÜLKE, U. (1968b). *Z. Anorg. Chem.* **360**, 231–246.
 SCHÜLKE, U., AVERBUCH-POUCHOT, M. T. & DURIF, A. (1992). In preparation.

Acta Cryst. (1992). **C48**, 1176–1179

Structure of Dibismuth Vanadate Bi₂VO_{5.5}

BY MARCEL TOUBOUL*

Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211, Université de Picardie, 33 rue Saint-Leu, 80039 Amiens CEDEX, France

JAN LOKAJ

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, 81237 Bratislava, Czechoslovakia

LAURENT TESSIER

Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211, Université de Picardie, 33 rue Saint-Leu, 80039 Amiens CEDEX, France

VIKTOR KETTMAN

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojarov 10, 81234 Bratislava, Czechoslovakia

AND VIKTOR VRABEL

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, 81237 Bratislava, Czechoslovakia

(Received 22 July 1991; accepted 2 December 1991)

Abstract. Bi₂VO_{5.5}, $M_r = 556.9$, orthorhombic, $Aba2$, $a = 5.598$ (2), $b = 15.292$ (9), $c = 5.532$ (2) Å, $V = 473.6$ Å³, $Z = 4$, $D_m = 7.6$, $D_x = 7.808$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 75.75$ mm⁻¹, $F(000) = 932$, $T = 293$ K, $R = 0.038$ for 396 unique observed reflections. Owing to a very short Bi—O bond (1.89 Å), the structure may be described by alternating Bi₂O_{2.75}⁵⁺ layers of very irregular corner-sharing BiO₄ tetrahedra and by VO_{2.75}^{0.5-} layers of distorted corner-sharing VO₆ octahedra. This structure is slightly different from that of well known oxides of the Aurivillius family and especially of Bi₂XO₆ com-

pounds ($X = \text{Mo, W}$) containing Bi₂O₂²⁺ layers of edge-sharing BiO₄ square pyramids.

Introduction. In a previous work, Touboul & Vachon (1988) investigated a large part of the Bi₂O₃–V₂O₅ system which was being studied at almost the same time by Zhou (1988) and by Blinovskov & Fotiev (1987). Numerous compounds were found but it was sometimes difficult to assign them a correct formula. It would be interesting to determine their structure in order to explain their physical properties, especially their ferroelectricity, as was found by Bierlein & Sleight (1975) for BiVO₄. Single crystals of several

* Author to whom all correspondence should be addressed.