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Preparation and crystal structure of bismuth trisodium trimetaphosphate nonahydrate: $BiNa_3(P_3O_9)_2 \cdot 9H_2O$

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Abstract. Chemical preparation and crystal structure are given for a bismuth-sodium trimetaphosphate $BiNa_3(P_3O_9)_2 \cdot 9H_2O$. This double cyclophosphate is trigonal, $R\bar{3}c$, with: $a = b = 30.845(15)$, $c = 13.085(3)$ Å, $Z = 18$, $V = 10781(13)$ Å^3 and $D_x = 2.534$ g cm^{-3}. The crystal structure has been solved by Patterson methods and refined to $R = 0.028$ for 2191 *hkl*. It consists of P_3O_9 rings lying in (001) planes interconnected by BiO_8 dodecahedra along the $\vec{c}$ axis and cross-linked by helicoïdal chains of NaO_6 and NaO_7 polyhedra.

Water molecules take part into the coordination polyhedron of each associated cation. Their arrangement makes the structure quite unstable.

A series of rare earth-sodium trimetaphosphates $TNa_3(P_3O_9)_2, 9H_2O$ has been synthetized with T = Sm, Eu, Gd, Tb, Dy, Ho, Er and Y. X-ray analysis has shown these compounds to be isotypic with the title compound.

Introduction

Up to now, in the rare earth trimetaphosphate field only the simple trimetaphosphates of the type $TP_3O_9 \cdot 3H_2O$ and $TP_3O_9 \cdot 4H_2O$ were synthetized. The trihydrated salts cristallize for T = La, Ce and Pr (Bagieu-Beucher et al., 1971 a). Their crystal structure of hexagonal symmetry has been established for the cerium salt (Bagieu-Beucher et al., 1971 b). The second series occurs for T = La, Pr and Er (Birke and Kempe, 1973), but has not yet been identified by X-ray analysis.

As no double trimetaphosphate of rare earth elements was mentioned in the literature, we tried to prepare a series with the monovalent cation Na. Thus compounds of general formula $TNa_3(P_3O_9)_2 \cdot 9H_2O$ were obtained with T = Sm, Eu, Gd, Tb, Dy, Ho, Er, Y and Bi. An X-ray analysis showed that all these salts were isotypic. Owing to its high quality, a crystal of $BiNa_3(P_3O_9)_2 \cdot 9H_2O$ was chosen for the structural study.

Chemical preparation

Crystals of $BiNa_3(P_3O_9)_2 \cdot 9H_2O$ have been prepared at room temperature by introducing about 1 g $BiCl_3 \cdot 6H_2O$ into 15 cc of a saturated $Na_3P_3O_9$ solution. Few minutes later, rapidly growing small crystals can be observed under the microscope. After some hours, the liquid is filtrated and crystals of suitable size are rapidly washed and air dried. Elongated hexagonal prisms are usually obtained.

A series of rare earth-sodium trimetaphosphate nonahydrates $TNa_3(P_3O_9)_2 \cdot 9H_2O$ has been synthesized by the same method for T = Sm, Eu, Gd, Tb, Dy, Ho, Er and Y. Crystal data of the series will be published later.

Crystal structure determination

The experimental conditions concerning the intensity data collection and the crystal data used for the structural determination are listed in Table 1.

The intensities have been corrected for Lorentz and polarisation effects, but no correction for absorption has been applied ($\mu R = 0.26$). Classical methods have been employed for solving the crystal structure: three-dimensional Patterson function for the localization of the heaviest atoms, successive Fourier syntheses for locating P and O atoms and difference Fourier synthesis in order to reveal the water molecules.

Computations have been carried out with the Enraf-Nonius SDP programs (1979) and the atomic scattering factors, $\Delta f'$, and $\Delta f''$ taken from International Tables for X-ray Crystallography (1974). Full-matrix refinements on F have been performed with a unitary weighting scheme. The final refinement cycles converge to a R value of 0.028 for a set of 2191 reflexions such that: $F_o^2 \geq 16\,\sigma(F_o^2)$. The same R factor is 0.031 for a set of 2669 reflexions with $F_o^2 \geq 9\,\sigma(F_o^2)$.

Table 2 reports the final atomic coordinates[1].

[1] Additional material to this paper can be ordered referring to the no. CSD 52201, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 1. Parameters used for the X-ray data collection and the crystal structure determination.

Apparatus	Enraf-Nonius CAD4
Wavelength	Ag$K\bar{\alpha}$(0.5608 Å)
Monochromator	Graphite plate
Scan mode	ω
Theta range	3–25°
Crystal size	$0.12 \times 0.12 \times 0.12$ mm^3
μ(Ag$K\alpha$)	43 cm^{-1}
Scan width	1.20°
Scan speed	from 0.01 to 0.04° × s^{-1}
Number of collected reflexions	8911
Total background measurement	15 to 60 s
Intensity reference reflexions	$11.4.\bar{5}$ and $\bar{1}\bar{1}.\bar{4}.5$
Unit cell dimensions determined	$a = b = 30.845(15)$ Å
from 25 reflexions ($10.06 \theta < 10.75°$)	$c = 13.085(3)$ Å
V, Mw	10871 Å^3, 931.9
Z, Dx	18, 2.534 g · cm^{-3}
Space group	$R\bar{3}c$
Rhombohedral unit cell dimensions	$a_R = 18.335$ Å, $\alpha_R = 114.53°$

Table 2. $BiNa_3(P_3O_9)_2 \cdot 9H_2O$ final atomic coordinates with e.s.d.s in parentheses. B_{eq} (Å^2) calculated from $B_{eq} = 4/3 \sum_i \sum_j \beta_{ij}\, \vec{a}_i \cdot \vec{a}_j$.

Atom	x	y	z	B_{eq}
Bi	0.15596(1)	0.0000(0)	0.2500(0)	1.55(2)
P(1)	0.23767(7)	0.03679(7)	0.0286(1)	1.87(3)
P(2)	0.06807(7)	0.23708(7)	0.0381(2)	1.87(3)
P(3)	0.13550(7)	0.00165(7)	0.9810(1)	1.75(3)
Na(1)	0.4822(2)	0.0000(0)	0.2500(0)	5.0(1)
Na(2)	0.2996(3)	0.2473(3)	0.2877(7)	11.7(3)
O(E11)	0.2307(2)	0.0455(2)	0.1381(4)	2.19(8)
O(E12)	0.0476(2)	0.4480(2)	0.1916(4)	2.76(9)
O(L12)	0.3541(2)	0.4433(2)	0.1818(4)	2.21(9)
O(E21)	0.2655(2)	0.4420(2)	0.5191(4)	2.24(9)
O(E22)	0.3865(2)	0.1661(2)	0.3263(5)	2.6(1)
O(L23)	0.6130(2)	0.1454(2)	0.3626(4)	2.05(8)
O(E31)	0.5626(2)	0.2268(2)	0.2286(4)	2.9(1)
O(E32)	0.5487(2)	0.2122(2)	0.4203(4)	1.93(8)
O(L13)	0.2957(2)	0.4732(2)	0.1301(4)	1.54(8)
O(W1)	0.1595(3)	0.2767(3)	0.2575(7)	5.1(2)
O(W2)	0.5294(2)	0.2673(2)	0.0858(5)	4.8(1)
O(W3)	0.3446(3)	0.2670(3)	0.0926(8)	7.7(2)
O(W4)	0.7791(5)	0.0000(0)	0.2500(0)	8.0(2)
O(W5)	0.0000(0)	0.3571(6)	0.2500(0)	10.0(3)
O(W6)	0.6722(5)	0.0000(0)	0.2500(0)	12.1(4)

Structure description

1. Trimetaphosphate anion

Figure 1 shows a partial (001) projection of the anionic arrangement around the $\bar{3}$ axis located at the origin of the unit cell.

Table 3 reports the main interatomic distances and bond angles in the P_3O_9 anion. This ring is quite regular with P–P–P angles close to 60° and P–P distances ranging from 2.818 to 2.848 Å. Average P–O distances are 1.549, 1.545 and 1.539 Å for the three tetrahedra. All these values are quite usual in trimetaphosphates.

In the (001) planes, six P_3O_9 rings are distributed around each 3 axis at three levels in the hexagonal cell ($z \approx 0$, 1/3, 2/3). Under each such ring ($z \approx 1/6$, 1/2, 5/6) there is an analogous one which is related to the upper one by a twofold axis. So, P_3O_9 rings form arrays running along the $\vec{c}$ direction.

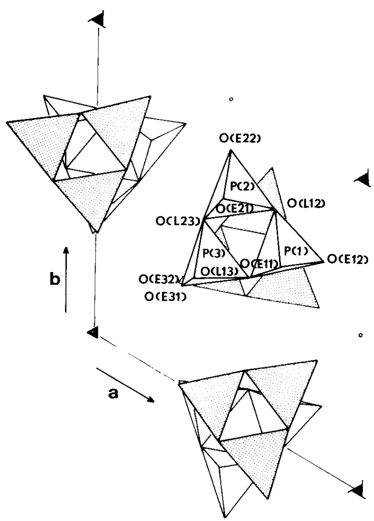

Fig. 1. Projection down $\vec{c}$ of some P_3O_9 rings lying at the level $z = 0$ and 1/2. White and stippled superimposed tetrahedra are related by a twofold axis.

Table 3. Main interatomic distances (Å) and bond angles (°) in the P_3O_9 ring anion. Standard deviations in parentheses.

P(1)	O(E11)	O(L12)	O(L13)	O(E12)
O(E11)	1.492(2)	108.6(2)	107.7(2)	122.1(2)
O(L12)	2.523(4)	1.610(3)	101.1(2)	106.2(2)
O(L13)	2.514(3)	2.492(4)	1.618(3)	109.1(2)
O(E12)	2.598(3)	2.470(4)	2.522(4)	1.476(2)
P(2)	O(E21)	O(L12)	O(L23)	O(E22)
O(E21)	1.482(2)	109.2(2)	108.8(2)	119.9(2)
O(L12)	2.520(4)	1.608(3)	100.6(2)	107.9(2)
O(L23)	2.516(3)	2.478(4)	1.612(3)	108.8(2)
O(E22)	2.563(4)	2.498(4)	2.514(4)	1.479(3)
P(3)	O(E31)	O(L13)	O(L23)	O(E32)
O(E31)	1.479(3)	108.7(2)	108.2(2)	118.4(2)
O(L13)	2.501(4)	1.598(3)	101.9(2)	109.6(2)
O(L23)	2.488(4)	2.476(3)	1.591(3)	108.8(2)
O(E32)	2.546(3)	2.521(3)	2.502(3)	1.486(3)
P(1)–P(2)	2.848(1)	P(1)–O(L12)–P(2)		124.5(2)
P(1)–P(3)	2.826(1)	P(1)–O(L13)–P(3)		123.0(2)
P(2)–P(3)	2.818(1)	P(2)–O(L23)–P(3)		123.2(2)
P(2)–P(1)–P(3)	59.55(3)			
P(1)–P(2)–P(3)	59.84(3)			
P(1)–P(3)–P(2)	60.61(3)			

Table 4. Main interatomic distances (Å) in cation polyhedra. Standard deviations in parentheses.

BiO_8 dodecahedron			
Bi–O(E11)	2.488(2) × 2		
Bi–O(E21)	2.497(2) × 2		
Bi–O(E32)	2.413(2) × 2		
Bi–O(W2)	2.378(3) × 2		
Na(1)O_6 octahedron		*Na(2)O_7 polyhedron*	
		Na(2)–O(E12)	2.568(5)
		Na(2)–O(E12)	2.453(5)
Na(1)–O(E12)	2.324(3) × 2	Na(2)–O(W1)	2.503(6)
Na(1)–O(E22)	2.311(3) × 2	Na(2)–O(W3)	2.823(7)
Na(1)–O(W1)	2.738(4) × 2	Na(2)–O(W4)	2.197(7)
		Na(2)–O(W5)	2.370(7)
		Na(2)–O(W6)	2.237(7)
Na(1)–Na(2)	3.114(5)	Na(1)–P(2)	3.376(2)
Na(2)–Na(2)	2.964(8)	Na(2)–P(1)	3.496(4)
O(W1)–O(W4)	3.132(4)	O(W3)–O(W6)	2.998(5)
O(W3)–O(W5)	2.751(8)	O(W4)–O(W6)	3.298(11)
O(W3)–O(W6)	3.331(7)	O(W5)–O(W6)	2.280(3)

2. Environments of the associated cations

A partial projection of the cation polyhedra arrangement can be seen in Fig. 2 while the main interatomic distances in these polyhedra are given in Table 4.

a) **Bi**. The bismuth atom is located on the twofold axis near each $\bar{3}$ axis. The geometry of its environment is a slightly distorted dodecahedron built up by six oxygen atoms and two water molecules O(W2) lying at the same level z as Bi. Bi – O distances vary from 2.378 to 2.497 Å. This type of eight-coordinated bonding is characteristic in Bi compounds which are isotypic with rare earth phosphates as the hexagonal modification of $BiPO_4$ (Mooney-Slater, 1962), the variety II of BiP_5O_{14} (Bagieu et al., 1973) or $KBi(PO_3)_4$ (Palkina, 1976).

BiO_8 dodecahedra are isolated and form (001) layers alternating with the P_3O_9 ones. Along a P_3O_9 array, the dodecahedral cavities are only

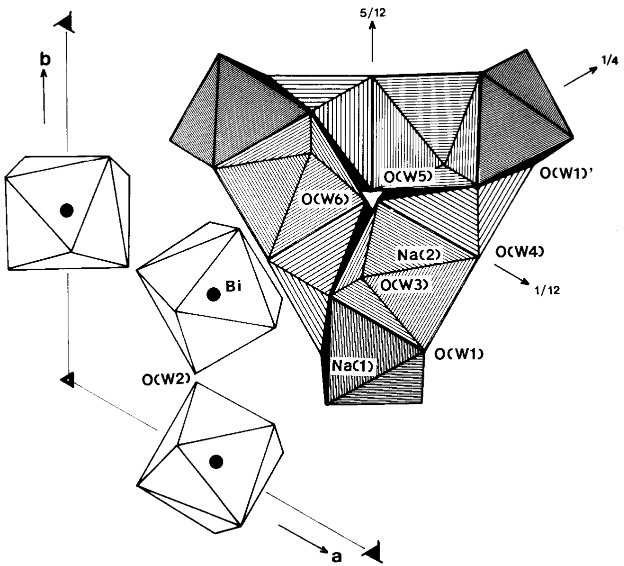

Fig. 2. Projection down $\vec{c}$ of the associated cation polyhedra in relation with Fig. 1. Some BiO_8 dodecahedra lying about $z = 1/4$ and 3/4 are represented. The chain built up of NaO_6 and NaO_7 hatched polyhedra is seen parallel to its direction. Phosphorus atoms have been omitted.

1/2 filled by the Bi atoms. Around each $\bar{3}$ axis, these arrays consisting of $P_3O_9 - BiO_8 - P_3O_9 - \square O_8$ periods delimite wide channels the effective aperture diameter of which varies from 3.7 (on the level of oxygen atoms) to 4.6 Å (on the level of water molecules).

The shortest distances Bi – Bi are 8.33 Å in a (001) plane, 8.12 Å between the nearest neighbouring Bi planes.

b) **Na**. The sodium cations are distributed on two sites near each 3_1 or 3_2 screw axis: Na(1) on the twofold axis and Na(2) in general position, respectively on levels similar to those of Bi and P atoms.

Na(1) atom is coordinated by four oxygen atoms at about 2.32 Å and two water molecules O(W1) at 2.74 Å forming a tetragonally distorted octahedron.

The coordination of Na(2) site is much more irregular with seven Na – O distances ranging from 2.20 to 2.82 Å. The distortion is probably due to the presence of five water molecules in the environment. Nevertheless,

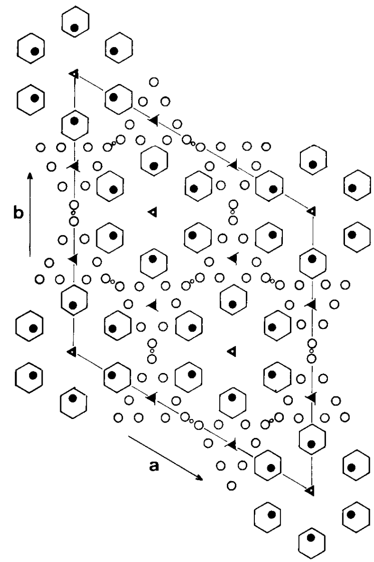

Fig. 3. Schematic projection of $BiNa_3(P_3O_9)_2 \cdot 9H_2O$ down $\vec{c}$ · P_3O_9 rings are shown as hexagons. Empty and filled circles indicate Na and Bi atoms respectively. Water molecules are not represented.

every distorted octahedron around Na(2), as shown in Fig. 2, contains two oxygen atoms and four water molecules O(W1), O(W3), O(W4), O(W6) (Fig. 2).

$Na(1)O_6$ and $Na(2)O_7$ polyhedra are connected together sharing common edges and faces so as to form helicoïdal chains along the 3_1 or 3_2 axes. The period of such a chain is composed of nine polyhedra. The shortest Na – Na distance in the column is 2.998 Å.

Moreover, the Na polyhedra columns separate the P_3O_9 rings related by the translations of the hexagonal cell.

c) $\mathbf{H_2O}$. As Bi and Na(1) atoms, the sites of the six water molecules lie in (001) planes between the P_3O_9 layers.

The part played by the water molecules is quite important in this structure. They participate in all the associated cation environments. The channels around the $\bar{3}$ axes are covered inside by the O(W2) of the Bi dodecahedra and outside by O(W1), O(W3) and O(W4) of Na polyhedra. Lastly O(W5) and O(W6) are bound together and form a screw-like column wreathing very near the helicoïdal axis with a pseudo-period O(W5) – O(W6) of 2.280 Å. This rather short distance between two water molecules is possible if their large thermal motion is considered.

3. Structural arrangement

A general view of the crystal structure is pictured by a schematic projection (Fig. 3). Around each $\bar{3}$ axis appear wide empty channels delimited by $P_3O_9 - BiO_8$ arrays. Around each screw axis, $NaO_6 - NaO_7$ columns try to maintain cohesion between these arrays in spite of numerous water molecules.

The high temperature factor which affects some Na atoms and water molecules in this structure are very often observed in highly hydrated compounds, mainly for non-bonded water molecules. This high factor is difficult to interpret: is it due to a wide potential to vibrate or is it simply a crystallographic site partly occupied? In the present compound the first hypothesis is probably the right one since weight losses at high temperature always indicated nine water molecules.

References

Bagieu, M., Tordjman, I., Durif, A., Bassi, G.: Holmium ultraphosphate, HoP_5O_{14}. Cryst. Struct. Commun. **3** (1973) 387 – 390.

Bagieu-Beucher, M., Durif, A.: Données cristallographiques sur trois trimétaphosphates de terres rares du type $TP_3O_9 \cdot 3H_2O$ (T = La, Ce et Pr). Bull. Soc. Fr. Minéral. Cristallogr. **94** (1971 a) 440 – 441.

Bagieu-Beucher, M., Tordjman, I., Durif, A.: Structure cristalline du trimétaphosphate de cérium(III)trihydraté: $CeP_3O_9 \cdot 3H_2O$. Rev. Chim. Miner. **8** (1971 b) 753 – 760.

Birke, P., Kempe, G.: Zum thermischen Verhalten der Phosphate einiger Selten-Erdmetalle: Lanthantrimetaphosphat-hydrat $La(P_3O_9) \cdot 4H_2O$. Z. Chem. **13**, Nr. 2, (1973) 65 – 66; Praesodymtrimetaphosphat-hydrat $Pr(P_3O_9) \cdot 4H_2O$. Z. Chem. **13**, Nr. 3 (1973) 110 – 111; Erbiumtrimetaphosphat-hydrat $Er(P_3O_9) \cdot 4H_2O$. Z. Chem. **13**, Nr. 4, (1973) 151 – 152.

Enraf-Nonius: Structure determination package. Enraf-Nonius, Delft (1979).

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

Mooney-Slater, R. C. L.: Polymorphic forms of Bismuth phosphate. Z. Kristallogr. **117** (1962) 371 – 385.

Palkina, K. K., Kuznetsov, V. G., Chudinova, N. N., Chibiskova, N. I.: Crystal structure of $KNd(PO_3)_4$. Dokl. Chem. **226** (1976) 46 – 48.