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Crystal Structure of a Barium–Zinc Decametaphosphate $Ba_2Zn_3P_{10}O_{30}$

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Barium–zinc decametaphosphate, $Ba_2Zn_3P_{10}O_{30}$, is monoclinic, $P2/n$, with the unit cell parameters a = 21.738(15), b = 5.356(5), c = 10.748(8) Å, β = 99.65(3)° and Z = 2. The crystal structure was solved with a final R value of 0.041. This salt provides the first structural evidence for the existence of a 10-phosphorus ring anion.

Introduction

During a systematic investigation of compounds existing in the $M^{II}(PO_3)_2$–$M^{II}(PO_3)_2$ systems a zinc–barium salt $Ba_2Zn_3P_{10}O_{30}$ was characterized. Its crystal structure provides the first evidence for the existence of a 10-phosphorus ring anion, $P_{10}O_{30}$. Chemical preparation, thermal stability, and crystal data for this salt have already been reported by the authors (*1*). The present work deals with the detailed crystal structure of this compound.

Crystal Structure

(*a*) *Experimental.* The crystal selected for the data collection was an irregular prism fragment (0.13 × 0.20 × 0.24 mm³). A set of 4618 independent reflections was collected in a range of 3 to 35° (Θ). A Philips PW 1100 automatic diffractometer operating with Mo$K\alpha$ radiation monochromatized by a graphite plate was used for this measurement. An ω-scan mode was used and each reflection was explored in an angular domain of 1.2° at a constant speed of 0.02° sec^{-1}. Background was measured for 10 sec at each extremity of the scan domain. Two standard reflections (020 and 0$\bar{2}$0) had no significant variations during the data collection. Corrections were applied for Lorentz and polarization effects but not for absorption.

(*b*) *Crystal structure determination.* Classical methods were used for the crystal structure determination. A few cations were located by using a three-dimensional Patterson function and then successive Fourier syntheses allowed us to localize the totality of the atomic framework. For the final refinement cycles 2759 reflections such that $F > 3\sigma_F$ were used leading to a final R value of 0.041. A unitary weighting scheme

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TABLE I

ATOMIC COORDINATES AND B_{eq} (Å^2) FOR $Ba_2Zn_3P_{10}O_{30}$ ($B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$)

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	B_{eq}
Ba	0.57580(2)	0.4983(1)	0.18736(4)	0.60
Zn(1)	0.5000(0)	0.5000(0)	0.5000(0)	0.71
Zn(2)	0.2500(0)	0.4514(2)	0.7500(0)	0.53
Zn(3)	0.2500(0)	0.5307(2)	0.2500(0)	0.66
P(1)	0.42580(9)	0.0939(4)	0.0552(2)	0.51
P(2)	0.47814(7)	−0.0158(4)	0.3173(2)	0.40
P(3)	0.37042(8)	−0.2145(4)	0.4134(2)	0.48
P(4)	0.30431(8)	−0.0444(8)	0.6222(2)	0.38
P(5)	0.20406(9)	0.2234(4)	0.4789(2)	0.47
O(L12)	0.4595(3)	−0.078(1)	0.1694(5)	0.58
O(L23)	0.4140(2)	−0.007(1)	0.3666(5)	0.80
O(L34)	0.3504(3)	−0.056(1)	0.5249(6)	1.35
O(L45)	0.2356(2)	−0.032(1)	0.5395(5)	0.75
O(L51)	0.3586(3)	0.116(1)	0.0979(5)	0.88
O(E11)	0.4544(3)	0.348(1)	0.0586(6)	1.06
O(E12)	0.4211(3)	−0.050(1)	−0.0653(5)	1.28
O(E21)	0.5051(3)	0.240(1)	0.3365(5)	0.88
O(E22)	0.5168(3)	−0.234(1)	0.3692(5)	0.78
O(E31)	0.3162(3)	−0.245(1)	0.3108(7)	1.57
O(E32)	0.4066(3)	−0.439(1)	0.4620(6)	1.12
O(E41)	0.3180(3)	0.195(1)	0.6918(6)	0.87
O(E42)	0.3093(3)	−0.283(1)	0.6950(6)	0.79
O(E51)	0.2433(3)	0.317(1)	0.3896(6)	1.31
O(E52)	0.1908(3)	0.394(1)	0.5809(5)	0.72

was used throughout the crystal structure determination. Table I reports the atomic coordinates and the calculated B_{eq}.[1]

Description of the Structure

(1) *Decametaphosphate Anion*

In the unit cell, two $P_{10}O_{30}$ rings are related by an inversion center. Each ring has a two-fold axis perpendicular to its mean plane (010). Its dimensions are about 11 × 10 Å in this plane and 5 Å along its symmetry axis. The puckered conformation of the ring looks like a "cradle," in contrast to

TABLE II

BOND LENGTHS (Å) AND BOND ANGLES (°) IN THE $P_{10}O_{30}$ RING

P(1)	O(E11)	O(L12)	O(L51)	O(E12)
O(E11)	1.492(3)	111.6(2)	108.6(2)	117.2(2)
O(L12)	2.565(4)	1.609(3)	98.3(2)	108.9(2)
O(L51)	2.518(4)	2.433(4)	1.607(3)	110.6(2)
O(E12)	2.550(4)	2.526(4)	2.551(4)	1.495(3)
P(2)	O(E21)	O(L12)	O(L23)	O(E22)
O(E21)	1.491(3)	110.8(2)	106.1(2)	118.9(2)
O(L12)	2.551(4)	1.608(3)	104.4(1)	103.9(2)
O(L23)	2.449(4)	2.515(4)	1.574(2)	111.9(2)
O(E22)	2.569(4)	2.443(4)	2.540(4)	1.492(3)
P(3)	O(E31)	O(L23)	O(L34)	O(E32)
O(E31)	1.482(3)	106.4(2)	109.7(2)	118.8(2)
O(L23)	2.464(4)	1.594(3)	96.8(2)	111.6(2)
O(L34)	2.510(5)	2.379(4)	1.588(3)	111.3(2)
O(E32)	2.551(4)	2.545(4)	2.536(4)	1.482(3)
P(4)	O(E41)	O(L34)	O(L45)	O(E42)
O(E41)	1.489(3)	105.8(2)	109.4(2)	118.9(2)
O(L34)	2.438(4)	1.566(3)	105.8(2)	108.5(2)
O(L45)	2.527(4)	2.530(4)	1.606(3)	107.7(2)
O(E42)	2.567(4)	2.482(4)	2.502(4)	1.492(3)
P(5)	O(E51)	O(L45)	O(L51)	O(E52)
O(E51)	1.475(3)	107.4(2)	109.1(2)	118.2(2)
O(L45)	2.494(4)	1.619(3)	100.0(2)	110.1(2)
O(L51)	2.487(4)	2.449(4)	1.578(3)	110.5(2)
O(E52)	2.546(4)	2.550(4)	2.523(4)	1.492(3)

P(1)–P(2)	2.915(1)	P(1)–O(L12)–P(2)	130.0(2)
P(2)–P(3)	2.915(1)	P(2)–O(L23)–P(3)	133.8(2)
P(3)–P(4)	3.002(1)	P(3)–O(L34)–P(4)	144.3(2)
P(4)–P(5)	2.838(1)	P(4)–O(L45)–P(5)	123.3(2)
P(5)–P(1)	2.870(1)	P(5)–O(L51)–P(1)	128.6(2)

P(5)–P(1)–P(2)	112.95(4)
P(1)–P(2)–P(3)	102.09(4)
P(2)–P(3)–P(4)	131.90(4)
P(3)–P(4)–P(5)	99.67(4)
P(4)–P(5)–P(1)	126.63(4)

[1] See NAPS document No. 03966 for 22 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $8.35 for up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE III

MAIN GEOMETRICAL FEATURES IN $(P_nO_{3n})^{n-}$ ANIONS WITH $n > 4$

Ref.	Cyclophosphates	S.G.	Ring symmetry	P–O ring (Å)	P–O exocyclic (Å)	O/P/O ring (°)	O/P/O exocyclic (°)	P/O/P range (°)
(3)	$NH_4Na_4P_5O_{15} \cdot 4H_2O$	$P\bar{1}$	1	1.595	1.470	100.9	120.2	120–134
(4)	$Na_6P_6O_{18} \cdot 6H_2O$	$Ccma$	$2/m$	1.613	1.471	99.2	120.7	125–131
(5)	$Cr_2P_6O_{18}$	$P2_1/a$	$\bar{1}$ + pseudo m	1.583	1.475	101.5	118.4	132–139
(6)	$Cu_2Li_2P_6O_{18}$	$P\bar{1}$	Pseudo m	1.587	1.485	99.2	118.3	131–141
(7)	$Cs_2(UO_2)_2P_6O_{18}$	$P2_1/n$	$\bar{1}$	1.589	1.469	100.3	119.2	129–132
(8)	$(NH_4)_2Cu_3P_8O_{24}$	$P\bar{1}$	$\bar{1}$	1.587	1.485	100.7	117.7	129–146
(9)	$K_2Ga_2P_8O_{24}$	$A2/m$	$2/m$	1.594	1.483	99.1	117.1	123–136
	$Ba_2Zn_3P_{10}O_{30}$	$P2/n$	2	1.595	1.488	101.1	118.4	123–144

most other cyclophosphate anions which are rather chair-shaped. Figure 1 gives a perspective view of the decametaphosphate unit produced by ORTEP (*2*).

Table II reports interatomic distances and angles in the $P_{10}O_{30}$ ring. Table III shows the average values of P–O distances and O–P–O angles in PO_4 tetrahedra, along with the ranges of P–O–P ring angles, for the cyclophosphate anions $(P_nO_{3n})^{n-}$ with $n > 4$. From this table, one can observe that the difference in conformation has no obvious effect on the bond lengths or angles. All these geometrical features are similar to those found in PO_4 tetrahedra linked to two other ones.

(2) *Environments of the Cations*

The geometry of Ba and Zn environments is described in Table IV.

(*a*) *Zn.* One of the main features of this structure is the coexistence of two different coordinations for the zinc atoms.

The zinc cations are distributed on three sites in special positions. Two of them, Zn(1) and Zn(2), have a slightly distorted octahedral coordination of oxygen atoms,

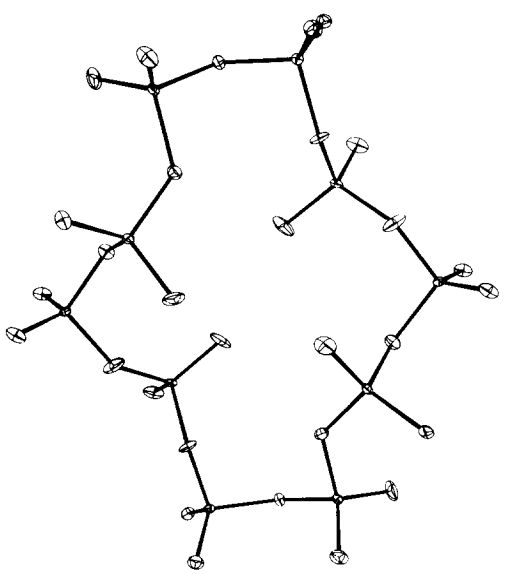

FIG. 1. Perspective view of the $P_{10}O_{30}$ anion.

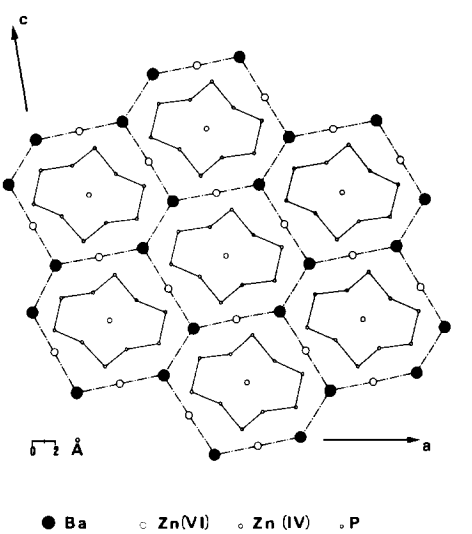

FIG. 2. Schematic projection of $Ba_2Zn_3P_{10}O_{30}$ down the **b** axis.

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE CATIONIC ENVIRONMENTS

$Zn(1)O_6$ octahedron

Zn(1)	O(E21)	O(E22)	O(E32)	O(E32')	O(E22')	O(E21')
O(E21)	2.260(3)	81.9(1)	96.9(1)	83.1(1)	98.1(1)	180
O(E22)	2.846(4)	2.077(3)	92.1(1)	87.9(1)	180	98.1(1)
O(E32)	3.214(5)	2.956(4)	2.029(3)	180	87.9(1)	83.1(1)
O(E32')	2.849(4)	2.850(4)	4.059(6)	2.029(3)	92.1(1)	96.9(1)
O(E22')	3.277(4)	4.154(6)	2.850(4)	2.956(4)	2.077(3)	81.9(1)
O(E21')	4.519(6)	3.277(6)	2.849(4)	2.214(5)	2.846(4)	2.260(3)

Zn(1)–P(2)	3.377(1)	Zn(1)–O(E21)–P(2)	127.2(2)
Zn(1)–P(2')	3.240(1)	Zn(1)–O(E22)–P(2')	129.7(2)
Zn(1)–P(3)	3.203(1)	Zn(1)–O(E32)–P(3)	131.0(2)

$Zn(2)O_6$ octahedron

Zn(2)	O(E41)	O(E42)	O(E52)	O(E52')	O(E41')	O(E42')
O(E41)	2.185(3)	82.3(1)	90.3(1)	78.9(1)	102.1(2)	175.4(1)
O(E42)	2.804(4)	2.073(3)	100.2(1)	91.6(1)	175.4(1)	93.2(2)
O(E52)	3.016(4)	3.175(4)	2.066(3)	162.9(2)	78.9(1)	91.6(1)
O(E52')	2.702(4)	2.967(4)	4.086(5)	2.066(3)	90.3(1)	100.2(1)
O(E41')	3.399(6)	4.253(4)	2.702(4)	3.016(4)	2.185(3)	82.3(1)
O(E42')	4.253(4)	3.013(6)	2.967(4)	3.175(4)	2.804(4)	2.073(3)

Zn(2)–P(4)	3.298(1)	Zn(2)–O(E41)–P(4)	126.7(2)
Zn(2)–P(4')	3.334(1)	Zn(2)–O(E42)–P(4')	138.0(2)
Zn(2)–P(5)	3.163(1)	Zn(2)–O(E52)–P(5)	124.7(2)

$Zn(3)O_4$ tetrahedron

Zn(3)	O(E31)	O(E51)	O(E51')	O(E31')
O(E31)	1.904(3)	105.1(1)	119.6(2)	101.8(2)
O(E51)	3.029(5)	1.911(3)	106.6(2)	119.6(2)
O(E51')	3.297(5)	3.063(6)	1.911(3)	105.1(1)
O(E31')	2.955(6)	3.297(5)	3.029(5)	1.904(3)

Zn(3)–P(3)	3.203(1)	Zn(3)–O(31)–P(3)	141.8(2)
Zn(3)–P(5)	3.253(1)	Zn(3)–O(51)–P(5)	147.5(2)

Environment of the Ba atoms

Ba–O(E11)	2.883(3)	Ba–O(E22)	2.892(3)
Ba–O(E11')	2.742(3)	Ba–O(E41)	2.951(3)
Ba–O(E12)	2.744(3)	Ba–O(E42)	2.848(3)
Ba–O(E12')	3.237(3)	Ba–O(E52)	2.975(3)
Ba–O(E21)	2.770(3)		
Ba–P(1)	3.397(1)	Ba–Zn(1)	3.983(0)
Ba–Ba	4.757(0)	Ba–Zn(2)	3.743(0)

the Zn–O bond lengths ranging between 2.03 and 2.26 Å. The third site, Zn(3), lying on the twofold axis of the ring, is tetrahedrally coordinated. The Zn–O distances are equal within 3σ and average 1.980 Å. On the other hand, the O–Zn–O angles ranging from 105 to 120° display more significant deviations from the average 109.6°. This

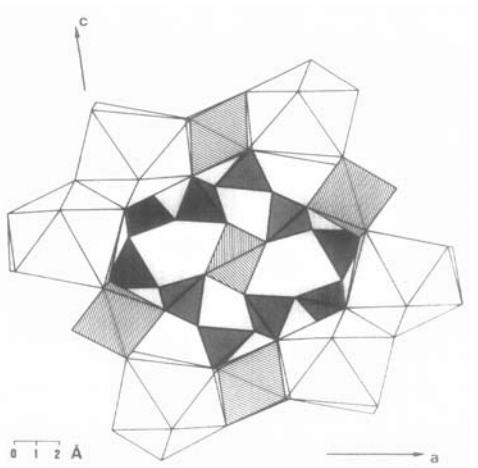

FIG. 3. Detailed projection of $Ba_2Zn_3P_{10}O_{30}$ down the **b** axis: $P_{10}O_{30}$ rings and ZnO_4 tetrahedra are situated inside of a channel built up with BaO_9 polyhedra and ZnO_6 hatched octahedra.

distorsion is also observed in other zinc phosphates (*10, 11*).

(*b*) *Ba.* The barium atoms situated in general positions are surrounded by nine oxygen atoms with a spread in the Ba–O distances from 2.74 to 3.24 Å. This ninefold coordination can best be described as resembling a deformed monocapped square antiprism.

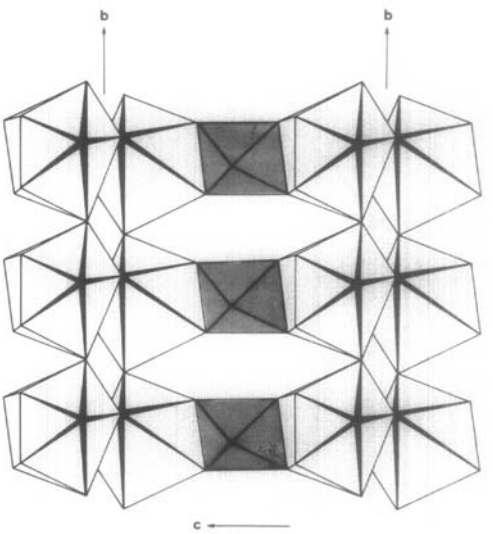

FIG. 4. Double arrays of BaO_9 polyhedra connected together by ZnO_6 octahedra.

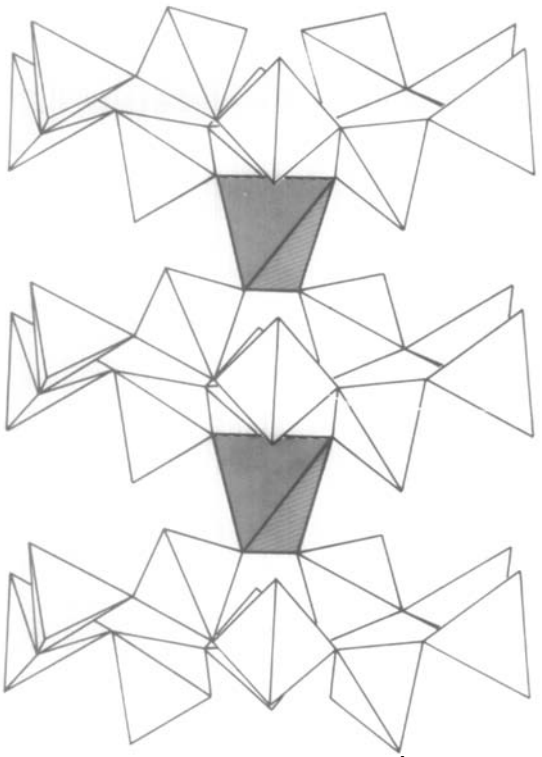

FIG. 5. Arrays of alternating $P_{10}O_{30}$ rings and ZnO_4 tetrahedra along the **b** axis.

(3) *Structural Arrangement*

Figure 2 represents a schematic projection of the whole arrangement down the **b** axis. In particular, we can recognize the cyclic anion with the tetrahedral zinc at the center on the twofold axis and the octahedral zinc linked to the Ba polyhedra outside the ring.

In fact, these Ba polyhedra are connected together along the third dimensions **b**, in such a way that they form, together with Zn octahedra, large channels in which are located the $P_{10}O_{30}$ rings and the Zn tetrahedra. The geometry of the section of such a channel is depicted in Fig. 3, while one of its faces is pictured in Fig. 4. So, double arrays of Ba polyhedra sharing edges and corners are running along the **b** axis. The arrays are cross-linked by Zn octahedra, through edge-sharing along **c** and through face-sharing along (**a** + **c**).

Figure 5 reveals the filling of a channel, which consists of $P_{10}O_{30}$ rings alternating with Zn tetrahedra, to form arrays along the twofold axis. In other words, the 10-membered rings of P tetrahedra are separated from each other by Zn tetrahedra in this one-dimensional way and by the channels themselves in a three-dimensional way.

In conclusion, $Ba_2Zn_3P_{10}O_{30}$ is not the highest member in the class of tetrahedron-ring systems: 12-tetrahedron ring anions have been characterized in the silicate and germanate domains (*12, 13*). Nevertheless, it is worthwhile noticing that $P_{10}O_{30}$ is the only 10-tetrahedron ring anion synthesized and identified so far.

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