

The layered polyphosphide

$\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$

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Received 15 October 2012; accepted 5 November 2012

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{P-P}) = 0.001$ Å; disorder in main residue; R factor = 0.018; wR factor = 0.042; data-to-parameter ratio = 23.4.

The silver zinc hexadecaphosphide $\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$ is the first polyphosphide in the ternary system Ag/Zn/P. It was synthesized from stoichiometric mixtures of Ag, Zn and P in the molar ratio 4:2:16, using AgI as a mineralizing agent in a gas-phase-assisted reaction. $\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$ crystallizes in the $\text{Cu}_5\text{InP}_{16}$ structure type. The asymmetric unit contains two Ag/Zn sites with mixed occupancies and four P sites. One of the Ag/Zn sites is located on a twofold rotation axis. The polyanionic $[\text{P}_{16}]$ -substructure consists of corrugated six-membered rings that are connected into a layer *via* the 1-, 2-, 4- and 5-positions of the rings by a bridging P atom in each case. The layers extend parallel to the bc plane and are stacked along the a axis. Both Ag/Zn sites are tetrahedrally coordinated by P atoms.

Related literature

For background to and structures of related polyphosphides, see: Bawohl & Nilges (2009); Dommann *et al.* (1989); Edmunds & Qurashi (1951); Lange *et al.* (2008); Möller & Jeitschko (1981); Olofsson (1965); Zanin *et al.* (2003). For background to the extinction correction, see: Becker & Coppens (1974).

Experimental

Crystal data

$\text{Ag}_{3.73}\text{Zn}_{2.27}\text{P}_{16}$	$V = 831.5$ (2) Å ³
$M_r = 1046.3$	$Z = 2$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.492$ (1) Å	$\mu = 9.05$ mm ⁻¹
$b = 9.9604$ (8) Å	$T = 293$ K
$c = 7.7106$ (9) Å	$0.02 \times 0.02 \times 0.02$ mm
$\beta = 109.585$ (9)°	

Data collection

IPDS Stoe 2T diffractometer	4398 measured reflections
Absorption correction: numerical (<i>X-AREA</i> ; Stoe & Cie, 2011)	1265 independent reflections
$T_{\min} = 0.730$, $T_{\max} = 0.771$	1135 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	54 parameters
$wR(F^2) = 0.042$	$\Delta\rho_{\text{max}} = 0.56$ e Å ⁻³
$S = 1.39$	$\Delta\rho_{\text{min}} = -0.66$ e Å ⁻³
1265 reflections	

Data collection: *X-AREA* (Stoe & Cie, 2011); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The authors thank the German Science Foundation (DFG) for the kind support of project NI1095/1–2.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2694).

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supporting information

Acta Cryst. (2012). E68, i91 [doi:10.1107/S1600536812045667]

The layered polyphosphide $\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$

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S1. Comment

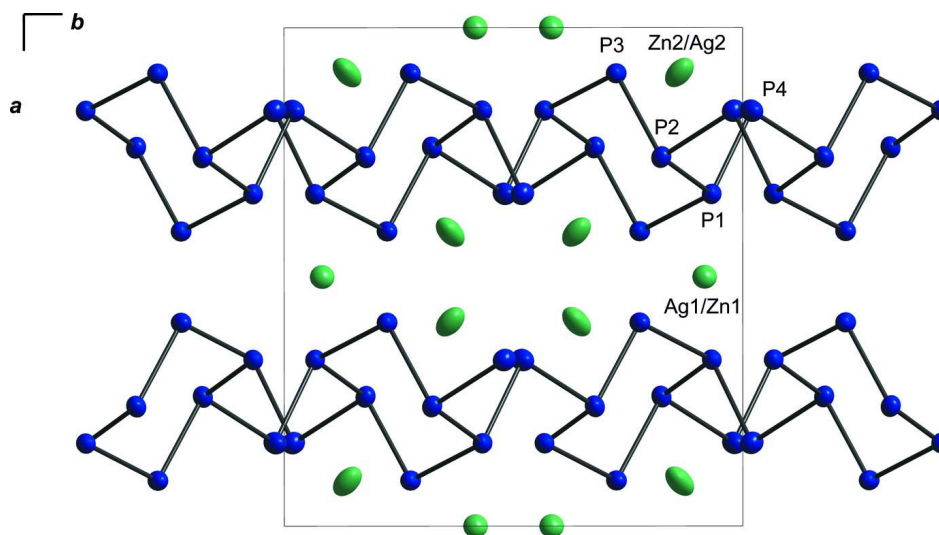
Herein we report on $\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$ (silver zinc hexadecaphosphide), the first ternary compound in the system Ag/Zn/P. It crystallizes isostructurally to $\text{Cu}_5\text{InP}_{16}$ in space group $C2/c$ (Lange *et al.*, 2008). The asymmetric unit is built up by two mixed-occupied Ag/Zn sites and four P sites. Both Ag/Zn sites are tetrahedrally coordinated by four P atoms featuring bond lengths of 2.4386 (7) to 2.5432 (7) Å. The bond lengths of the (Ag1/Zn1) site to phosphorus range from 2.4386 (7) to 2.4836 (7) Å while slightly longer bond lengths of 2.4551 (7) to 2.5432 (7) Å are observed for (Ag2/Zn2). This finding is consistent with the higher amount of zinc on the (Ag1/Zn1) site leading to somewhat shorter bond lengths. For comparison, Zn—P bond length range from 2.36 to 2.40 Å in ZnP_2 (Zanin *et al.*, 2003) and ZnP_4 (Dommann *et al.*, 1989) while common Ag—P distances in polyphosphides are observed from 2.47 to 2.61 Å in Ag_3P_{11} (Möller & Jeitschko, 1981) and 2.50 to 2.69 Å in AgP_2 (Olofsson, 1965), respectively. Mixed-occupied Ag/Zn sites are not uncommon and are observed, for example, in intermetallic phases like $\text{Ag}_{4.5}\text{Zn}_{4.5}$ (or better AgZn; Edmunds & Qurashi, 1951). All P—P distances in $\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$, ranging from 2.1909 (9) to 2.2328 (9) Å, are within the expected range for polyphosphides (Bawohl & Nilges, 2009).

S2. Experimental

$\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$ was prepared by reaction from the elements Ag (ChemPur, powder, 99.9%), Zn (Sigma-Aldrich, pices, 99.9%), and P (ChemPur, powder, 99.999%) in the stoichiometric ratio of 4:2:16 in a 500 mg batch. As mineralizing agent, 10 mg AgI (ChemPur, powder, 99.9%) per 500 mg total sample weight was added. The reaction was carried out in evacuated ampoules in a muffle furnace at 823 K during 14 days using a heating ratio of 70 K/h. The sample was cooled down slowly at a rate of 5 K/h. For X-ray powder phase analyses a fraction of the sample was ground. Phase purity has been substantiated. Single crystals of suitable size for a single-crystal structure determination could be separated from the bulk phase. The sample was stable under atmospheric conditions for months.

S3. Refinement

The mixed-occupied Ag/Zn sites are located on Wyckoff positions 4*e* and 8*f*. The refinement of the Ag and Zn content was constrained to an overall full occupancy according to the sum of the two elements, each of them located on the same coordinates and with the same displacement parameters. The ratio of the two elements has been refined unrestricted.

**Figure 1**

The crystal structure of $\text{Ag}_{3.73(4)}\text{Zn}_{2.27(4)}\text{P}_{16}$, viewed along the c axis. The mixed Ag/Zn sites are drawn in turquoise and P atoms in blue, respectively. The displacement ellipsoids are shown at the 90% probability level.

Silver zinc hexadecaphosphide

Crystal data

$\text{Ag}_{3.73}\text{Zn}_{2.27}\text{P}_{16}$

$M_r = 1046.3$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 11.492(1)\ \text{\AA}$

$b = 9.9604(8)\ \text{\AA}$

$c = 7.7106(9)\ \text{\AA}$

$\beta = 109.585(9)^\circ$

$V = 831.5(2)\ \text{\AA}^3$

$Z = 2$

$F(000) = 966$

$D_x = 4.17\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4528 reflections

$\theta = 2.8\text{--}30.5^\circ$

$\mu = 9.05\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Isomorphous, black

$0.02 \times 0.02 \times 0.02\ \text{mm}$

Data collection

IPDS Stoe 2T

diffractometer

Radiation source: X-ray tube

Plane graphite monochromator

Detector resolution: $6.67\ \text{pixels mm}^{-1}$

rotation method scans

Absorption correction: numerical

($X\text{-AREA}$; Stoe & Cie, 2011)

$T_{\min} = 0.730$, $T_{\max} = 0.771$

4398 measured reflections

1265 independent reflections

1135 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 30.5^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -16 \rightarrow 16$

$k = -13 \rightarrow 14$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.042$

$S = 1.39$

1265 reflections

54 parameters

0 restraints

14 constraints

Weighting scheme based on measured s.u.'s $w =$

$1/(\sigma^2(I) + 0.0004I^2)$

$(\Delta/\sigma)_{\max} = 0.038$

$\Delta\rho_{\max} = 0.56\ \text{e \AA}^{-3}$

$$\Delta\rho_{\min} = -0.66 \text{ e } \text{\AA}^{-3}$$

Extinction correction: B-C type 1 Gaussian
isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.084 (5)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ag1	0	0.41699 (3)	0.25	0.01075 (10)	0.422 (6)
Zn1	0	0.41699 (3)	0.25	0.01075 (10)	0.578 (6)
Ag2	-0.089927 (17)	0.13768 (2)	-0.08750 (3)	0.01608 (7)	0.721 (7)
Zn2	-0.089927 (17)	0.13768 (2)	-0.08750 (3)	0.01608 (7)	0.279 (7)
P1	-0.16624 (5)	0.56752 (5)	0.05996 (7)	0.00731 (15)	
P2	-0.24029 (5)	0.32264 (5)	-0.24701 (7)	0.00785 (15)	
P3	0.09157 (4)	0.27552 (6)	0.07194 (7)	0.00827 (15)	
P4	-0.33325 (5)	0.48032 (5)	-0.14361 (8)	0.00915 (15)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.01067 (15)	0.01146 (16)	0.01117 (17)	0	0.00506 (10)	0
Zn1	0.01067 (15)	0.01146 (16)	0.01117 (17)	0	0.00506 (10)	0
Ag2	0.01637 (11)	0.01572 (12)	0.01331 (12)	-0.00637 (6)	0.00121 (7)	-0.00034 (6)
Zn2	0.01637 (11)	0.01572 (12)	0.01331 (12)	-0.00637 (6)	0.00121 (7)	-0.00034 (6)
P1	0.0079 (2)	0.0074 (2)	0.0071 (2)	0.00021 (16)	0.00310 (17)	0.00069 (17)
P2	0.0090 (2)	0.0076 (2)	0.0072 (2)	-0.00064 (16)	0.00309 (17)	-0.00022 (18)
P3	0.0077 (2)	0.0082 (2)	0.0093 (3)	0.00004 (16)	0.00342 (18)	0.00121 (17)
P4	0.0096 (2)	0.0104 (2)	0.0080 (2)	-0.00069 (17)	0.00363 (17)	-0.00171 (18)

Geometric parameters (\AA , $^\circ$)

Ag1—P1	2.4836 (7)	Ag2—P4 ⁱⁱⁱ	2.5280 (7)
Ag1—P1 ⁱ	2.4836 (7)	P1—P2 ^{iv}	2.2328 (9)
Ag1—P3	2.4385 (7)	P1—P3 ^v	2.1909 (9)
Ag1—P3 ⁱ	2.4385 (7)	P1—P4	2.2095 (9)
Ag2—P2	2.5432 (7)	P2—P3 ^{vi}	2.1976 (8)
Ag2—P3	2.4551 (7)	P2—P4	2.1941 (9)
Ag2—P4 ⁱⁱ	2.5115 (7)		
P1—Ag1—P1 ⁱ	105.73 (2)	Ag2—P2—P4	132.64 (3)
P1—Ag1—P3	114.11 (2)	P1 ^{vii} —P2—P3 ^{vi}	104.18 (3)
P1—Ag1—P3 ⁱ	106.81 (2)	P1 ^{vii} —P2—P4	103.43 (3)
P1 ⁱ —Ag1—P3	106.81 (2)	P3 ^{vi} —P2—P4	96.77 (3)
P1 ⁱ —Ag1—P3 ⁱ	114.11 (2)	Ag1—P3—Ag2	98.66 (2)
P3—Ag1—P3 ⁱ	109.40 (2)	Ag1—P3—Zn2	98.66 (2)
P2—Ag2—P3	99.36 (2)	Ag1—P3—P1 ^v	99.15 (3)
P2—Ag2—P4 ⁱⁱ	93.38 (2)	Ag1—P3—P2 ^{viii}	110.66 (3)
P2—Ag2—P4 ⁱⁱⁱ	109.66 (2)	Ag2—P3—P1 ^v	124.46 (3)
P3—Ag2—P4 ⁱⁱ	140.08 (2)	Ag2—P3—P2 ^{viii}	119.19 (3)

P3—Ag2—P4 ⁱⁱⁱ	110.23 (2)	P1 ^v —P3—P2 ^{viii}	102.39 (3)
P4 ⁱⁱ —Ag2—P4 ⁱⁱⁱ	100.52 (2)	Ag2 ^{ix} —P4—Ag2 ⁱⁱⁱ	139.72 (3)
Ag1—P1—P2 ^{iv}	106.99 (3)	Ag2 ^{ix} —P4—Zn2 ⁱⁱⁱ	139.72 (3)
Ag1—P1—P3 ^v	111.18 (3)	Ag2 ^{ix} —P4—P1	108.81 (3)
Ag1—P1—P4	119.67 (3)	Ag2 ^{ix} —P4—P2	103.06 (3)
P2 ^{iv} —P1—P3 ^v	104.82 (3)	Ag2 ⁱⁱⁱ —P4—Zn2 ^{ix}	139.72 (3)
P2 ^{iv} —P1—P4	103.40 (3)	Ag2 ⁱⁱⁱ —P4—P1	96.17 (3)
P3 ^v —P1—P4	109.44 (3)	Ag2 ⁱⁱⁱ —P4—P2	104.53 (3)
Ag2—P2—P1 ^{vii}	109.17 (3)	P1—P4—P2	97.28 (3)
Ag2—P2—P3 ^{vi}	107.16 (3)		

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $-x-1/2, y-1/2, -z-1/2$; (iii) $-x-1/2, -y+1/2, -z$; (iv) $x, -y+1, z+1/2$; (v) $-x, -y+1, -z$; (vi) $x-1/2, -y+1/2, z-1/2$; (vii) $x, -y+1, z-1/2$; (viii) $x+1/2, -y+1/2, z+1/2$; (ix) $-x-1/2, y+1/2, -z-1/2$.