

Cs₂Bi(PO₄)(WO₄)Kateryna V. Terebilenko,^{a*} Igor V. Zatovsky,^a
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Received 17 July 2009; accepted 10 August 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(W-O) = 0.009$ Å; R factor = 0.052; wR factor = 0.115; data-to-parameter ratio = 22.9.

Dicaesium bismuth(III) phosphate(V) tungstate(VI), Cs₂Bi(PO₄)(WO₄), has been synthesized during complex investigation in a molten pseudo-quaternary Cs₂O–Bi₂O₃–P₂O₅–WO₃ system. It is isotypic with K₂Bi(PO₄)(WO₄). The three-dimensional framework is built up from [Bi(PO₄)(WO₄)] nets, which are organized by adhesion of [BiPO₄] layers and [WO₄] tetrahedra above and below of those layers. The interstitial space is occupied by Cs atoms. Bi, W and P atoms lie on crystallographic twofold axes.

Related literature

For the isotypic potassium analogue, see: Zatoovsky *et al.* (2006). For a related structure, see: Terebilenko *et al.* (2008). For caesium coordination, see Borel *et al.* (2000); Yakubovich *et al.* (2006)

Experimental*Crystal data*

Cs ₂ Bi(PO ₄)(WO ₄)	$V = 1923.21$ (14) Å ³
$M_r = 817.61$	$Z = 8$
Orthorhombic, <i>Ibca</i>	Mo $K\alpha$ radiation
$a = 21.3144$ (10) Å	$\mu = 37.87$ mm ⁻¹
$b = 12.6352$ (5) Å	$T = 293$ K
$c = 7.1412$ (3) Å	$0.08 \times 0.07 \times 0.05$ mm

Data collection

Oxford Diffraction XCalibur-3 diffractometer	10697 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	1396 independent reflections
$T_{\min} = 0.061$, $T_{\max} = 0.174$ (expected range = 0.053–0.151)	1227 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.156$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	61 parameters
$wR(F^2) = 0.115$	$\Delta\rho_{\text{max}} = 2.17$ e Å ⁻³
$S = 1.21$	$\Delta\rho_{\text{min}} = -2.63$ e Å ⁻³
1396 reflections	

Table 1

Selected bond lengths (Å).

Bi1–O2	2.388 (8)	Cs1–O4 ^{vii}	3.140 (9)
Bi1–O1 ⁱ	2.389 (8)	Cs1–O1	3.338 (9)
Bi1–O3 ⁱⁱ	2.463 (8)	Cs1–O3 ^{vii}	3.339 (9)
Bi1–O1 ⁱⁱⁱ	2.669 (8)	W1–O4	1.774 (9)
Cs1–O2 ⁱⁱ	2.990 (8)	W1–O3 ^{vi}	1.792 (9)
Cs1–O4 ^{iv}	3.031 (9)	P1–O1	1.539 (8)
Cs1–O2 ⁱ	3.046 (8)	P1–O1 ⁱⁱ	1.539 (8)
Cs1–O3 ^v	3.088 (9)	P1–O2 ⁱⁱ	1.549 (8)
Cs1–O4 ^{vi}	3.111 (10)		

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y, -z$; (iii) $x, y - \frac{1}{2}, -z$; (iv) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $x, -y + 1, -z + \frac{1}{2}$; (vii) $x, y + \frac{1}{2}, -z$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

The authors acknowledge the ICDD for financial support (grant No. 03–02).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2113).

References

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supplementary materials

Acta Cryst. (2009). E65, i67 [doi:10.1107/S160053680903147X]

Cs₂Bi(PO₄)(WO₄)

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Comment

Chemistry of caesium phosphates shows a great diversity due to its structural flexibility in adopting different coordination environment. In metal phosphates caesium resides generally in complex polyhedron with up to fourteen vertices providing formation of two- and three-dimensional frameworks. Depending on crystal structure caesium is believed to occupy big cavities and tunnels adapting their geometry. For instance, the structure of Cs₃Mo₈O₁₁(PO₄)₈ (Borel *et al.*, 2000) represents two types of irregular surrounding with nine and ten oxygen coordination, Cs₂Ti(VO₂)₃(PO₄)₃ (Yakubovich *et al.*, 2006) - twelve and fourteen. Herein, the structure of K₂Bi(PO₄)(WO₄) (Zatovsky *et al.*, 2006) represents an interesting host for substitution of potassium atoms by caesium ones, that leads to formation of the first example of caesium-containing phosphate-tungstate Cs₂Bi(PO₄)(WO₄) (Fig 1). Three-dimensional framework of the title compound is organized by linking together [Bi(PO₄)(WO₄)] nets which are formed by adhesion [BiPO₄] layers and WO₄ tetrahedra above and below of those layers (Fig. 2). Both phosphate and tungstate tetrahedra have almost regular geometry with typical bond lengths. Caesium atom resides in interlayer space having eightfold coordination duplicating potassium ones' environment in the structure of K₂Bi(PO₄)(WO₄) (Zatovsky *et al.*, 2006). Due to bigger ionic radius of Cs, the distance between two successive nets (a half of a cell dimension *a*) is 10.657 Å, while for K-analogue is 9.862 Å.

Experimental

Single crystals of the title compound were obtained during investigation in the pseudo-quaternary molten system Cs₂O—Bi₂O₃—P₂O₅—WO₃. A mixture of CsPO₃ (1.060 g), Cs₂W₂O₇ (3.725 g) and Bi₂O₃ (0.840 g) were mixed in an agate mortar, and heated in a platinum crucible up to 1223 K to obtain a homogeneous melt. It was held at this temperature for an hour and cooled down with a rate of 40 K h⁻¹ to 833 K. Crystalline product was leached out from the solidified melt with hot water.

Refinement

Convergence factors (*R*, *wR*) and *R*_{int} are high due to low intensity of the reflections which is connected with poor quality of crystals. Experiments were carried out for several crystals from different synthetic points, unfortunately, better results than is presented were not found. Taking into account the previous structures isotypic to titled compound there is no doubts in structure determination.

The highest peak and the deepest hole in the final difference map are located at 0.77 Å from P1 (2.173 e/Å³) and 0.70 Å from P2 (-2.633 e/Å³) respectively.

Figures

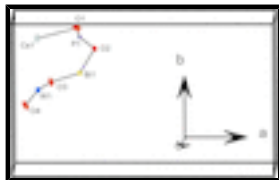


Fig. 1. View of the title compound with displacement ellipsoids at the 50% probability level.

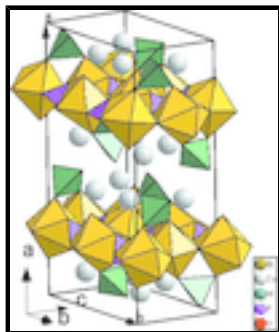


Fig. 2. View of $\text{Cs}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$.

Dicaesium bismuth(III) phosphate(V) tungstate(VI)

Crystal data

$\text{Cs}_2\text{Bi}(\text{PO}_4)(\text{WO}_4)$

$M_r = 817.61$

Orthorhombic, *Ibca*

Hall symbol: $-I\ 2b\ 2c$

$a = 21.3144\ (10)\ \text{\AA}$

$b = 12.6352\ (5)\ \text{\AA}$

$c = 7.1412\ (3)\ \text{\AA}$

$V = 1923.21\ (14)\ \text{\AA}^3$

$Z = 8$

$F_{000} = 2768$

$D_x = 5.648\ \text{Mg m}^{-3}$

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

Cell parameters from 10697 reflections

$\theta = 3.2\text{--}30.0^\circ$

$\mu = 37.87\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, colourless

$0.08 \times 0.07 \times 0.05\ \text{mm}$

Data collection

Oxford Diffraction XCalibur-3
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(Blessing, 1995)

$T_{\min} = 0.061$, $T_{\max} = 0.174$

10697 measured reflections

1396 independent reflections

1227 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.156$

$\theta_{\max} = 30.0^\circ$

$\theta_{\min} = 3.2^\circ$

$h = -27 \rightarrow 29$

$k = -17 \rightarrow 17$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 22.3992P]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.21$	$(\Delta/\sigma)_{\max} < 0.001$
1396 reflections	$\Delta\rho_{\max} = 2.17 \text{ e } \text{\AA}^{-3}$
61 parameters	$\Delta\rho_{\min} = -2.63 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.25	0.58662 (4)	0	0.01381 (17)
Cs1	0.09029 (3)	0.83471 (6)	0.21999 (11)	0.0233 (2)
W1	0.09279 (3)	0.5	0.25	0.01566 (18)
P1	0.25	0.8232 (3)	0	0.0081 (6)
O1	0.2413 (4)	0.8984 (6)	0.1675 (11)	0.0204 (17)
O2	0.3072 (4)	0.7487 (6)	0.0220 (11)	0.0173 (15)
O3	0.1403 (4)	0.5328 (8)	0.0513 (13)	0.0258 (18)
O4	0.0440 (4)	0.3925 (8)	0.1847 (13)	0.031 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.0116 (3)	0.0135 (3)	0.0162 (3)	0	-0.00033 (18)	0
Cs1	0.0166 (4)	0.0290 (4)	0.0243 (4)	0.0014 (3)	-0.0003 (2)	0.0005 (3)
W1	0.0107 (3)	0.0162 (3)	0.0201 (3)	0	0	0.0007 (2)
P1	0.0077 (15)	0.0086 (13)	0.0080 (15)	0	-0.0014 (10)	0
O1	0.034 (5)	0.015 (3)	0.012 (4)	-0.004 (3)	0.002 (3)	-0.003 (3)
O2	0.013 (4)	0.017 (3)	0.021 (4)	-0.001 (3)	0.000 (3)	0.003 (3)
O3	0.013 (4)	0.036 (5)	0.028 (4)	-0.007 (4)	-0.004 (3)	0.006 (4)
O4	0.020 (5)	0.032 (5)	0.040 (5)	-0.013 (4)	0.007 (4)	-0.013 (4)

supplementary materials

Geometric parameters (Å, °)

Bi1—O2	2.388 (8)	Cs1—O4 ^{viii}	3.111 (10)
Bi1—O2 ⁱ	2.388 (8)	Cs1—O4 ^{ix}	3.140 (9)
Bi1—O1 ⁱⁱ	2.389 (8)	Cs1—O1	3.338 (9)
Bi1—O1 ⁱⁱⁱ	2.389 (8)	Cs1—O3 ^{ix}	3.339 (9)
Bi1—O3 ⁱ	2.463 (8)	W1—O4	1.774 (9)
Bi1—O3	2.463 (8)	W1—O4 ^{viii}	1.774 (9)
Bi1—O1 ^{iv}	2.669 (8)	W1—O3 ^{viii}	1.792 (9)
Bi1—O1 ^v	2.669 (8)	W1—O3	1.792 (9)
Cs1—O2 ⁱ	2.990 (8)	P1—O1	1.539 (8)
Cs1—O4 ^{vi}	3.031 (9)	P1—O1 ⁱ	1.539 (8)
Cs1—O2 ⁱⁱ	3.046 (8)	P1—O2 ⁱ	1.549 (8)
Cs1—O3 ^{vii}	3.088 (9)	P1—O2	1.549 (8)
?—?—?	?		

Symmetry codes: (i) $-x+1/2, y, -z$; (ii) $-x+1/2, -y+3/2, -z+1/2$; (iii) $x, -y+3/2, z-1/2$; (iv) $x, y-1/2, -z$; (v) $-x+1/2, y-1/2, z$; (vi) $-x, y+1/2, -z+1/2$; (vii) $x, -y+3/2, z+1/2$; (viii) $x, -y+1, -z+1/2$; (ix) $x, y+1/2, -z$.

Fig. 1

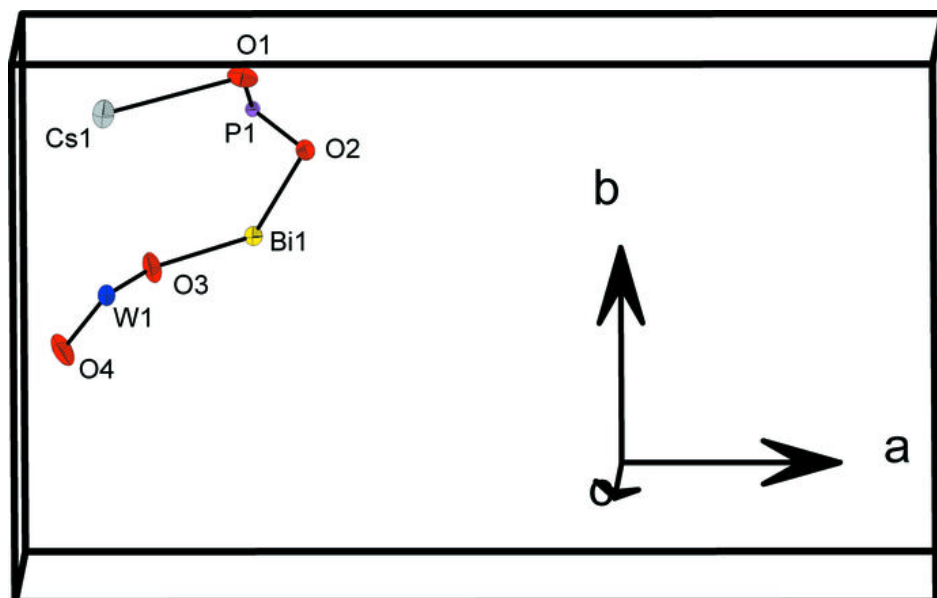


Fig. 2

