inorganic compounds

Barium zinc diarsenate

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The title compound, $BaZnAs_2O_7$, belongs to the family of isotypic series of compounds adopting the general formula $M1^{2+}M2^{2+}X_2O_7$ ($M1^{2+}$ = Ca, Sr, Ba or Pb; $M2^{2+}$ = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd; X = P or As). Suitable single crystals were prepared under hydrothermal conditions. The framework structure is characterized by corner-sharing ZnO_5 square pyramids and As_2O_7 groups where the Zn atoms occupy channels. X-ray diffraction analysis of single crystals twinned by non-merohedry [twin plane is (100)] yielded formula $BaZnAs_2O_7$. Raman spectra confirmed the presence of a non-linear As—O—As linkage.

Related literature

For isostructural diarsenates, see: Pertlik (1986); Horng & Wang (1994); Wardojo & Hwu (1995); Chen & Wang (1996); Mihajlović *et al.* (2004). For the relationship to the known $M1^{2+}M2^{2+}X_2O_7$ compounds and the presence of non-merohedral twinning, see: Mihajlović *et al.* (2004). For related literature, see: Staack & Müller-Buschbaum (1998); Mihajlović & Effenberger (2006); Murashova *et al.* (1991); Nord *et al.* (1988).

Experimental

Crystal data

$BaZnAs_2O_7$	V = 641.1 (2) Å^3
M_r = 464.55	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 5.6260 (10) Å	μ = 20.08 mm^{-1}
b = 8.557 (2) Å	T = 293 (2) K
c = 13.317 (3) Å	$0.09 \times 0.04 \times 0.02$ mm
β = 90.01 (3)°	

Data collection

Nonius KappaCCD diffractometer	11068 measured reflections
Absorption correction: multi-scan	2807 independent reflections
(Otwinowski & Minor, 1997)	2747 reflections with $I > 2\sigma(I)$
T_{min} = 0.265, T_{max} = 0.690	R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022	102 parameters
$wR(F^2)$ = 0.056	$\Delta\rho_{max}$ = 2.21 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −1.77 e Å^{-3}
2807 reflections	

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997; Otwinowski *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 1999); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2081).

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supporting information

Barium zinc diarsenate

Tamara Đorđević

S1. Comment

Diphosphates with the general formula $M1M2P_2O_7$ have been extensively studied during the last years. Among them are a couple of compounds with divalent M1 and M2 atoms (Mihajlović *et al.*, 2004 and references therein). These diphosphates show a variety of crystal structure types that are controlled by the distinct stereochemical behaviour of the M1 and M2 cations. It affects the coordination numbers, the degree of distortion of the coordination polyhedra, and the conformation of the P_2O_7 groups (Murashova *et al.*, 1991). By comparison much less is known about the structural chemistry of compounds with the formula $M1^{2+}M2^{2+}X_2O_7$ where X = V, Cr, Ge, As, and Si. Prior to this study, the crystal structures of only seven diarsenates $M1^{2+}M2^{2+}As_2O_7$ were known. Six of the first ones are isotypic with the title compound and crystallize in space group $P2_1/n$: $PbCuAs_2O_7$ (Pertlik, 1986), $SrCoAs_2O_7$ (Horng & Wang, 1994), $BaCuAs_2O_7$ (Wardojo & Hwu, 1995; Chen & Wang, 1996), $BaMgAs_2O_7$, $BaCoAs_2O_7$ (Mihajlović *et al.*, 2004) and $SrCuAs2O7$ (Chen & Wang, 1996). Worthy to note is the five-coordinated $M(2)$ position. $CaCuAs2O7$ has the same space-group symmetry; however, for the reduced cell the space group setting is $P2_1/c$ and the structural features are different (Chen & Wang, 1996; Staack & Müller-Buschbaum, 1998).

The crystal structure of $BaZnAs_2O_7$ is characterized by a three-dimensional framework formed from corner-sharing square pyramids ZnO_5 and As_2O_7 groups. Within the framework bent chains running parallel to [010] are formed by the ZnO_5 and $As1O_4$ polyhedra. They are linked by the $As2O_4$ tetrahedra. Each of the five corners of the square pyramids around the Zn atoms are shared with a different As_2O_7 group. The Ba position is located within channels parallel to [010] (Fig. 1). The Ba atoms are coordinated by nine oxygen atoms, and the coordination polyhedron can be described as a distorted tricapped trigonal prism. The average <Ba—O> bond length of 2.829 Å compare well to that of $BaMgAs_2O_7$, $BaCoAs_2O_7$ and $BaCuAs_2O_7$ (2.852, 2.829 and 2.852 Å, respectively). The pyroarsenate groups involve two crystallographically non-equivalent AsO_4 tetrahedra. As expected, the longest As—O bonds are to the bridging oxygen atoms: <As1—O1> = 1.746 (2) Å and <As2—O1> = 1.751 (3) Å. The bond angles $O_{terminal}$—As—$O_{terminal}$ are significantly larger than $O_{bridging}$—As—$O_{terminal}$. The As1—$O_{bridging}$—As2 angle is 124.67 (14)°.

In the 1000–800 cm^{-1} range, Raman spectrum shows the As—O antisymmetric and symmetric stretching modes of the $(As_2O_7)^{4-}$ groups [904 (sh), 892 (*vs*), 847 (*m*), 825 (*m*)]. The bands at 784 (w) and 585 (*s*) cm^{-1} can be assigned to the asymmetric [v_{as} (As—O—As)] and symmetric bridge stretching vibration [v_s (As—O—As)], respectively and they are characteristic of the $(As_2O_7)^{4-}$ group with a non-linear As—O—As bond (Nord *et al.*, 1988). In the region below 450 cm^{-1} appear the bending modes of the $(As_2O_7)^{4-}$ groups, and various lattice modes of the compound.

The presence of only two structure types among $M1^{2+}M2^{2+}$-diarsenates contrasts with the situation among the $M1^{2+}M2^{2+}$-diphosphates where a greater variety of structure types is known; however, it probably reflects to some extent the different number of diphosphates and diarsenates studied so far.

S2. Experimental

Single crystals of $BaZnAs_2O_7$ were obtained as reaction products from mixtures of $Ba(OH)_2\cdot 8H_2O$ (Merck, > 97%), $2ZnO\cdot 2CO_3\cdot 4H_2O$ (Alfa Products), and As_2O_5 (Alfa Products, > 99.9%). The mixture was transferred into Teflon vessel and filled to approximately 70% of their inner volume with distilled water (pH of the mixture was 2.5). Finally it was enclosed into stainless steel autoclave. The mixture was heated under autogeneous pressure from 293 to 493 K (4 h), held at that temperature (72 h) and rapidly cooled to room temperature. At the end of the reaction the pH of the solvent was 6. $BaZnAs_2O_7$ crystallizes as colourless, prismatic crystals up to 0.11 mm in length (yield *ca* 25%). It was obtained together with colourless, prismatic crystals of $Ba(AsO_3OH)$ (yield *ca* 60%) (Mihajlović & Effenberger, 2006) and uninvestigated amorphous mass yield *ca* 15%).

S3. Refinement

Several single crystals of the $BaZnAs_2O_7$ were studied with an automatic four-circle X-ray diffractometer equipped with a CCD area detector. Preliminary measurements showed sharp reflection spots and a pseudo-orthorhombic unit cell. However, closer inspections of the recorded CCD frames revealed that at higher diffraction angles some very slight splitting or slight broadening of the reflection spots was evident; this was later found to be due to twinning. The space-group symmetry was confirmed as $P2_1/n$ based on the extinction rules. It crystal structure was refined starting from the atomic coordinates given for $BaCuAs_2O_7$ (Chen & Wang, 1996). Although the structure models appeared to be crystal-chemically correct, the refinements initially converged unsatisfactorily. Distinct discrepancies between measured and calculated structure factors were observed ($F_{obs}^2 > F_{calc}^2$ for the most disagreeable reflections). The weighting scheme used by the programme *SHELXL97* (Sheldrick, 2008) suggested unexpectedly large values for the second weighting parameters. Furthermore, in the residual electron densities remained unusually high peaks which indicated the presence of 'phantom′ atoms apparently mirroring atom positions across the (100) plane. Because of the pseudo-orthorhombic metrics of the unit cells (β close to 90°), non-merohedric twinning with a twin plane parallel to (100) was assumed. The application of the twin matrix (-1 0 0, 0 1 0, 0 0 1) during the refinement procedures reduced the *R*-values significantly. During the last stages anisotropic displacement parameters were allowed to vary for all atoms.
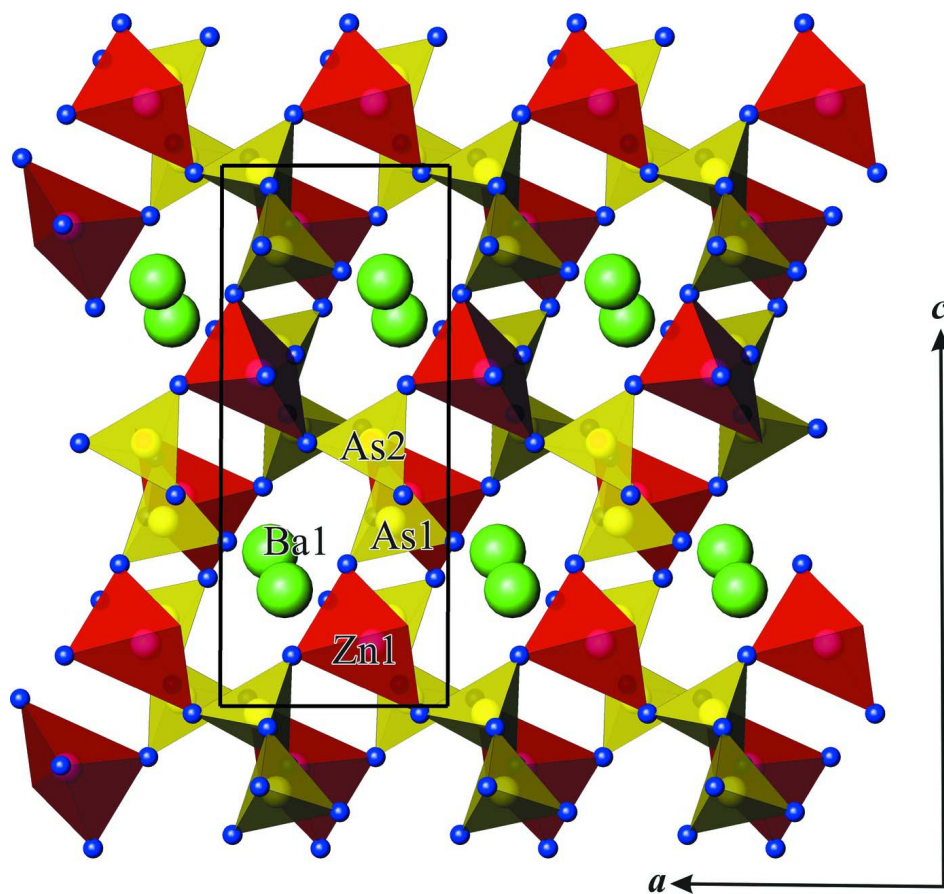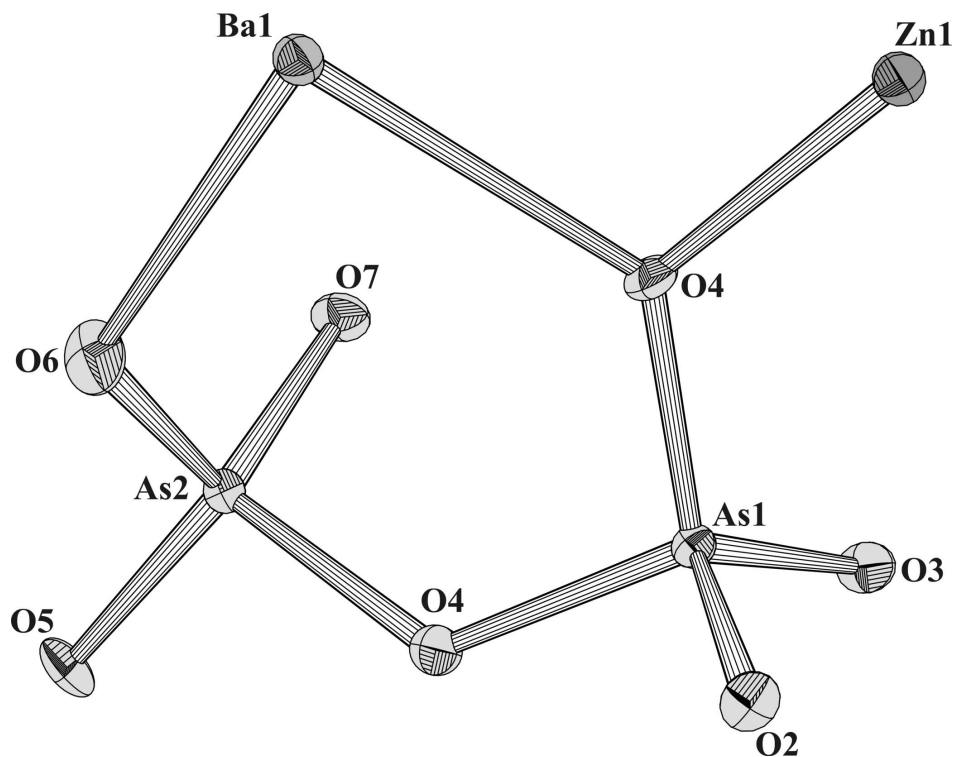
Figure 1

The crystal structure of BaZnAs$_2$O$_7$ in a projection parallel to [010].

Figure 2

Atomic displacement ellipsoids at the 50% probability level.

Barium zinc diarsenate

Crystal data

$BaZnAs_2O_7$	$F(000) = 832$
$M_r = 464.55$	$D_x = 4.813$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5551 reflections
$a = 5.626$ (1) Å	$\theta = 0.4$–$35.0°$
$b = 8.557$ (2) Å	$\mu = 20.08$ mm^{-1}
$c = 13.317$ (3) Å	$T = 293$ K
$\beta = 90.01$ (3)°	Prismatic, colourless
$V = 641.1$ (2) Å^3	$0.09 \times 0.04 \times 0.02$ mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	11068 measured reflections
Radiation source: fine-focus sealed tube	2807 independent reflections
Graphite monochromator	2747 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan (Otwinowski & Minor, 1997)	$\theta_{max} = 35.0°$, $\theta_{min} = 1.5°$
	$h = -9 \rightarrow 9$
	$k = -13 \rightarrow 13$
$T_{min} = 0.265$, $T_{max} = 0.690$	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 1.09P]$
$wR(F^2) = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2807 reflections	$\Delta\rho_{max} = 2.21$ e Å⁻³
102 parameters	$\Delta\rho_{min} = -1.77$ e Å⁻³
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]⁻¹ᐟ⁴
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0037 (3)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Ba1	0.21674 (4)	0.34610 (2)	0.715139 (16)	0.01062 (5)
Zn1	0.66892 (8)	0.14866 (4)	0.88747 (3)	0.01171 (8)
As1	0.75049 (6)	0.03337 (3)	0.65727 (2)	0.00781 (6)
As2	0.67177 (6)	0.31336 (4)	0.51369 (2)	0.00760 (6)
O1	0.7114 (5)	0.1140 (3)	0.53795 (18)	0.0143 (4)
O2	0.6667 (5)	−0.1533 (3)	0.6483 (2)	0.0130 (4)
O3	1.0297 (5)	0.0613 (3)	0.6914 (2)	0.0175 (5)
O4	0.5580 (4)	0.1208 (3)	0.73543 (19)	0.0111 (4)
O5	0.8103 (5)	0.3354 (3)	0.40399 (19)	0.0117 (4)
O6	0.3801 (5)	0.3486 (3)	0.5158 (2)	0.0114 (4)
O7	0.8042 (5)	0.4073 (3)	0.60893 (18)	0.0131 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba1	0.01013 (8)	0.01003 (8)	0.01171 (8)	0.00076 (5)	−0.00048 (7)	−0.00098 (5)
Zn1	0.01165 (17)	0.01094 (16)	0.01254 (16)	−0.00053 (12)	−0.00077 (14)	0.00057 (11)
As1	0.00859 (13)	0.00678 (12)	0.00807 (12)	0.00043 (9)	−0.00037 (11)	0.00005 (9)
As2	0.00792 (12)	0.00819 (12)	0.00668 (11)	−0.00004 (10)	−0.00003 (10)	0.00028 (9)
O1	0.0249 (13)	0.0089 (9)	0.0092 (9)	0.0013 (9)	−0.0022 (9)	0.0006 (7)
O2	0.0166 (11)	0.0048 (9)	0.0176 (11)	−0.0001 (8)	0.0022 (9)	−0.0011 (7)
O3	0.0091 (10)	0.0163 (11)	0.0270 (13)	−0.0004 (8)	−0.0051 (9)	0.0005 (10)
O4	0.0105 (10)	0.0133 (10)	0.0097 (9)	0.0012 (8)	0.0021 (7)	−0.0029 (8)
O5	0.0094 (10)	0.0162 (10)	0.0096 (10)	0.0000 (8)	0.0035 (8)	0.0014 (7)
O6	0.0087 (10)	0.0145 (10)	0.0110 (10)	0.0005 (7)	0.0000 (8)	−0.0022 (8)
O7	0.0172 (10)	0.0110 (9)	0.0111 (9)	−0.0013 (9)	−0.0075 (8)	−0.0008 (7)

Geometric parameters (Å, º)

Ba1—O3[i]	2.641 (3)	Zn1—O7[vi]	2.071 (3)
Ba1—O3[ii]	2.674 (3)	Zn1—O6[vii]	2.082 (3)
Ba1—O4	2.734 (3)	Zn1—O4	2.132 (3)
Ba1—O7[ii]	2.768 (3)	As1—O3	1.652 (3)
Ba1—O6	2.809 (3)	As1—O2	1.669 (2)
Ba1—O2[iii]	2.821 (3)	As1—O4	1.678 (2)
Ba1—O4[iii]	2.889 (3)	As1—O1	1.746 (2)
Ba1—O5[iv]	3.002 (3)	As2—O5	1.667 (3)
Ba1—O5[v]	3.157 (2)	As2—O6	1.669 (3)
Zn1—O2[i]	1.989 (2)	As2—O7	1.676 (2)
Zn1—O5[iv]	2.034 (3)	As2—O1	1.751 (2)
O3[i]—Ba1—O3[ii]	154.69 (6)	O5[iv]—Ba1—O5[v]	151.15 (6)
O3[i]—Ba1—O4	93.77 (8)	O2[i]—Zn1—O5[iv]	115.47 (11)
O3[ii]—Ba1—O4	69.23 (8)	O2[i]—Zn1—O7[vi]	145.21 (11)
O3[i]—Ba1—O7[ii]	124.18 (8)	O5[iv]—Zn1—O7[vi]	97.87 (11)
O3[ii]—Ba1—O7[ii]	77.40 (8)	O2[i]—Zn1—O6[vii]	85.52 (11)
O4—Ba1—O7[ii]	140.60 (7)	O5[iv]—Zn1—O6[vii]	118.44 (11)
O3[i]—Ba1—O6	105.27 (9)	O7[vi]—Zn1—O6[vii]	87.17 (10)
O3[ii]—Ba1—O6	91.37 (8)	O2[i]—Zn1—O4	90.21 (11)
O4—Ba1—O6	82.47 (7)	O5[iv]—Zn1—O4	79.64 (10)
O7[ii]—Ba1—O6	77.89 (8)	O7[vi]—Zn1—O4	86.10 (10)
O3[i]—Ba1—O2[iii]	96.19 (9)	O6[vii]—Zn1—O4	161.45 (10)
O3[ii]—Ba1—O2[iii]	77.12 (8)	O2[i]—Zn1—Ba1[viii]	142.43 (9)
O4—Ba1—O2[iii]	118.34 (7)	O5[iv]—Zn1—Ba1[viii]	59.85 (7)
O7[ii]—Ba1—O2[iii]	71.81 (8)	O7[vi]—Zn1—Ba1[viii]	48.98 (7)
O6—Ba1—O2[iii]	149.22 (8)	O6[vii]—Zn1—Ba1[viii]	130.97 (7)
O3[i]—Ba1—O4[iii]	67.32 (8)	O4—Zn1—Ba1[viii]	52.43 (7)
O3[ii]—Ba1—O4[iii]	123.92 (8)	O2[i]—Zn1—Ba1	77.81 (9)
O4—Ba1—O4[iii]	157.94 (3)	O5[iv]—Zn1—Ba1	51.31 (7)
O7[ii]—Ba1—O4[iii]	60.91 (7)	O7[vi]—Zn1—Ba1	120.23 (7)
O6—Ba1—O4[iii]	112.59 (7)	O6[vii]—Zn1—Ba1	150.26 (7)
O2[iii]—Ba1—O4[iii]	56.12 (7)	O4—Zn1—Ba1	44.28 (7)
O3[i]—Ba1—O5[iv]	82.60 (8)	O3—As1—O2	115.24 (14)
O3[ii]—Ba1—O5[iv]	72.34 (8)	O3—As1—O4	112.25 (14)
O4—Ba1—O5[iv]	55.22 (7)	O2—As1—O4	106.77 (13)
O7[ii]—Ba1—O5[iv]	132.28 (8)	O3—As1—O1	108.22 (15)
O6—Ba1—O5[iv]	137.57 (7)	O2—As1—O1	106.10 (13)
O2[iii]—Ba1—O5[iv]	66.11 (8)	O4—As1—O1	107.88 (13)
O4[iii]—Ba1—O5[iv]	108.88 (7)	O5—As2—O6	117.03 (14)
O3[i]—Ba1—O5[v]	70.18 (8)	O5—As2—O7	113.66 (13)
O3[ii]—Ba1—O5[v]	135.12 (8)	O6—As2—O7	109.72 (13)
O4—Ba1—O5[v]	133.79 (7)	O5—As2—O1	102.27 (12)
O7[ii]—Ba1—O5[v]	62.59 (7)	O6—As2—O1	107.34 (13)
O6—Ba1—O5[v]	62.25 (7)	O7—As2—O1	105.74 (12)

| O2ⁱⁱⁱ—Ba1—O5^v | 106.58 (7) | As1—O1—As2 | 124.67 (14) |
| O4ⁱⁱⁱ—Ba1—O5^v | 52.15 (7) | | |

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