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# An investigation of polyhedral deformation in two mixed-metal diarsenates: $SrZnAs_2O_7$ and $BaCuAs_2O_7$

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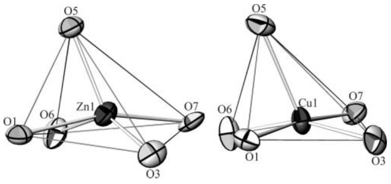
Two isostructural diarsenates, $SrZnAs_2O_7$ (strontium zinc diarsenate), (I), and $BaCuAs_2O_7$ [barium copper(II) diarsenate], (II), have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction. The three-dimensional open-framework crystal structure consists of corner-sharing $M2O_5$ ($M2$ = Zn or Cu) square pyramids and diarsenate ($As_2O_7$) groups. Each $As_2O_7$ group shares its five corners with five different $M2O_5$ square pyramids. The resulting framework delimits two types of tunnels aligned parallel to the [010] and [100] directions where the large divalent nine-coordinated $M1$ ($M1$ = Sr or Ba) cations are located. The geometrical characteristics of the $M1O_9$, $M2O_5$ and $As_2O_7$ groups of known isostructural diarsenates, adopting the general formula $M1^{II}M2^{II}As_2O_7$ ($M1^{II}$ = Sr, Ba, Pb; $M2^{II}$ = Mg, Co, Cu, Zn) and crystallizing in the space group $P2_1/n$, are presented and discussed.



## 1. Introduction

The structural properties of divalent cation diphosphates and diarsenates, $M_2^{II}X_2^{V}O_7$ ($M^{II}$ = divalent cation; $X^{V}$ = P, As) (Weil *et al.*, 2009; Edhokkar *et al.*, 2012), mixed-valence cation diphosphates and diarsenates, $M1^{I}M2^{III}X^{V}{}_{2}O_7$ (Kolitsch, 2004; Schwendtner & Kolitsch, 2004; Horchani-Naifer & Férid, 2007; Ouerfelli *et al.*, 2007; Rousse *et al.*, 2013) and $M1_2^{I}M2^{II}X_2^{V}O_7$ (Faggiani & Calvo, 1976; Marzouki *et al.*, 2012), and mixed-cation diphosphates with the general formula $M1^{II}M2^{II}P_2O_7$ ($M1^{II}$ = Ca, Sr, Ba, Pb; $M2^{II}$ = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd; references are given in the footnotes of Table 1) have been broadly investigated and described. Yet, reports on the $M1^{II}M2^{II}As_2O_7$ diarsenates are rather rare. Prior to this study, the structural data for only seven diarsenates have been reported, namely $SrCuAs_2O_7$ (Chen & Wang, 1996), $SrCoAs_2O_7$ (Horng & Wang, 1994), $PbCuAs_2O_7$ (Pertlik, 1986), $BaCuAs_2O_7$ (Wardojo & Hwu, 1995; Chen & Wang, 1996), $BaMgAs_2O_7$ and $BaCoAs_2O_7$ (Mihajlović *et al.*, 2004), and $BaZnAs_2O_7$ (Đorđević, 2008).

All known diphosphate and diarsenate $M1^{II}M2^{II}X_2O_7$ compounds, crystallizing in the monoclinic space group $P2_1/n$ with comparable pseudo-orthorhombic unit-cell dimensions $a \simeq 5.2$–$5.7$, $b \simeq 8.2$–$8.9$, $c \simeq 12.5$–$13.3$ Å and $\beta \simeq 90^\circ$, show a structural similarity to the $\alpha$-$Ca_2P_2O_7$ structure (Calvo, 1968). The structure of $\alpha$-$Ca_2P_2O_7$ is characterized by two crystallographically distinct eight-coordinated cationic sites occupied by Ca1 and Ca2. In the $\alpha$-$Ca_2P_2O_7$ isotype compounds $M1^{II}M2^{II}X_2O_7$, the $M1^{II}$ cation of larger radius occupies the Ca1 site, whereas the smaller $M2^{II}$ cation occupies the Ca2 site. The coordination numbers of $M1^{II}$ and $M2^{II}$ may vary

**Table 1**
Comparison of the unit-cell parameters (Å, °) for $M1^{II}M2^{II}X_2O_7$ compounds ($M1$ = $Ba^{2+}$, $Sr^{2+}$, $Pb^{2+}$, $Ca^{2+}$; $M2$ = $Cu^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cr^{2+}$; $X$ = $As^{5+}$, $P^{5+}$).

| Compound | *a* | *b* | *c* | *β* | *V* (Å$^3$) | ICSD (2014) reference |
|---|---|---|---|---|---|---|
| $SrCuAs_2O_7$[1] | 5.550 (1) | 8.299 (2) | 12.858 (2) | 91.75 (3) | 592.0 (2) | 82624 |
| $SrCoAs_2O_7$[2] | 5.520 (1) | 8.391 (2) | 13.083 (3) | 90.90 (2) | 605.9 (2) | 74545 |
| $SrZnAs_2O_7$[3] | 5.5114 (11) | 8.3524 (17) | 13.106 (3) | 91.01 (3) | 603.2 (2) | |
| $PbCuAs_2O_7$[4] | 5.553 (1) | 8.404 (1) | 13.011 (2) | 91.61 (2) | 606.95 (16) | 61339 |
| $BaCuAs_2O_7$[1] | 5.736 (1) | 8.458 (2) | 13.044 (3) | 91.16 (3) | 632.7 (2) | 82625 |
| $BaCuAs_2O_7$[3] | 5.7343 (11) | 8.4722 (17) | 13.071 (3) | 91.12 (3) | 634.9 (2) | |
| $BaCuAs_2O_7$[5] | 5.740 (5) | 8.475 (3) | 13.090 (3) | 91.24 (4) | 636.6 (6) | 80329 |
| $BaMgAs_2O_7$[6] | 5.620 (1) | 8.629 (2) | 13.344 (3) | 90.20 (3) | 647.1 (2) | |
| $BaCoAs_2O_7$[6] | 5.649 (1) | 8.577 (1) | 13.278 (2) | 90.014 (1) | 643.3 (2) | |
| $BaZnAs_2O_7$[7] | 5.6260 (10) | 8.557 (2) | 13.317 (3) | 90.01 (3) | 641.1 (2) | 260061 |
| $CaCuP_2O_7$[8] | 5.2104 (4) | 8.0574 (5) | 12.344 (1) | 91.356 (6) | 518.08 (7) | 68510 |
| $\alpha$-$Ca_2P_2O_7$[9] | 5.315 (5) | 8.542 (8) | 12.66 (1) | 90.3 (1) | 574.8 (9) | 22225 |
| $SrNiP_2O_7$[10] | 5.2691 (5) | 8.2674 (8) | 12.6140 (13) | 90.246 (9) | 549.48 (9) | 411740 |
| $SrCuP_2O_7$[11] | 5.369 (1) | 8.129 (1) | 12.455 (2) | 90.59 (1) | 543.56 (15) | 74445 |
| $SrMgP_2O_7$[12] | 5.3046 (8) | 8.3053 (13) | 12.700 (2) | 90.502 (3) | 559.48 (15) | 280782 |
| $SrCoP_2O_7$[13] | 5.3165 (4) | 8.2574 (5) | 12.6755 (7) | 90.133 (5) | 556.46 (6) | 69578 |
| $SrZnP_2O_7$[14] | 5.3143 (2) | 8.2080 (3) | 12.7250 (6) | 90.192 (4) | 555.06 (4) | |
| $SrZnP_2O_7$[15] | 5.30906 (2) | 8.21392 (3) | 12.73595 (5) | 90.1573 (3) | 555.390 (5) | 160198 |
| $SrFeP_2O_7$[16] | 5.370 (2) | 8.268 (4) | 12.693 (3) | 90.37 (2) | 563.5 (4) | 280078 |
| $SrCrP_2O_7$[17] | 5.422 (2) | 8.3254 (19) | 12.542 (4) | 90.39 (3) | 566.1 (3) | 280309 |
| $SrCdP_2O_7$[18] | 5.414 (1) | 8.615 (3) | 12.878 (5) | 90.01 (3) | 600.6 (4) | 72672 |
| $Sr_{1.34}Pb_{0.66}P_2O_7$[19] | 5.433 (4) | 8.944 (6) | 13.183 (6) | 90.12 (5) | 640.6 (7) | 75000 |
| $PbCuP_2O_7$[20] | 5.381 (1) | 8.194 (2) | 12.569 (1) | 90.39 (1) | 554.18 (18) | 79996 |
| $PbCoP_2O_7$[20] | 5.322 (1) | 8.292 (2) | 12.777 (2) | 90.18 (1) | 563.85 (19) | 79994 |
| $PbMnP_2O_7$[20] | 5.393 (1) | 8.461 (2) | 12.848 (3) | 90.00 (3) | 586.3 (2) | 79995 |
| $BaMgP_2O_7$[21] | 5.483 (1) | 8.561 (3) | 12.626 (2) | 91.32 (2) | 592.5 (3) | 39398 |
| $BaMnP_2O_7$[22] | 5.5537 (6) | 8.633 (2) | 12.825 (2) | 90.08 (1) | 614.90 (18) | 78657 |

References: (**1**) Chen & Wang (1996); (**2**) Horng & Wang (1994); (**3**) this work; (**4**) Pertlik (1986); (**5**) Wardojo & Hwu (1995); (**6**) Mihajlović *et al.* (2004); (**7**) Đorđević (2008); (**8**) Riou & Goreaud (1990); (**9**) Calvo (1968); (**10**) El Bali *et al.* (2001); (**11**) Moqine *et al.* (1993); (**12**) Tahiri *et al.* (2002); (**13**) Riou & Raveau (1991); (**14**) Höppe *et al.* (2007); (**15**) Yuan *et al.* (2007); (**16**) Le Meins & Courbion (1999); (**17**) Maass & Glaum (2000); (**18**) Alaoui El Belghiti *et al.* (1991); (**19**) Elmarzouki *et al.* (1994); (**20**) Elmarzouki *et al.* (1995); (**21**) Murashova *et al.* (1991); (**22**) Adams *et al.* (1995).

from 7 to 9 for $M1^{II}$ and from 5 to 9 for $M2^{II}$. The $X^{V}$ is the smallest tetrahedrally coordinated cation. The $X_2O_7^{4-}$ anion consists of two $XO_4$ tetrahedra sharing an O atom, denoted $O_b$, with a bridging bond angle $X—O_b—X$ of approximately 125°. Therefore, the structure of $M1^{II}M2^{II}X_2O_7$ compounds can be described as ionic with $M1^{II}$ and $M2^{II}$ as the cations and $X_2O_7^{4-}$ as the anion. Alternatively, the structure can be described as the complex compound $\{M1[M2(X_2O_7)]\}_n$, with $M2$ as a central metal cation surrounded by five $X_2O_7$ ligands. $M1$ serves as a counter-cation in order to produce electroneutrality. The structures of diarsenates $M1^{II}M2^{II}As_2O_7$ are characterized by a three-dimensional open framework formed from corner-sharing $M2O_5$ square pyramids and $As_2O_7$ groups. The framework contains two types of tunnels, *viz.* smaller pentagonal tunnels along the [100] direction and larger tunnels along the [010] direction, in which arrays of $M1^{II}$ cations are located.

The present article reports the hydrothermal synthesis and crystal structures of $SrZnAs_2O_7$ and $BaCuAs_2O_7$ based on single-crystal X-ray diffraction data. $SrZnAs_2O_7$ is a compound with a new chemical composition and the structure of $BaCuAs_2O_7$ has been redetermined. The lattice parameters obtained for $BaCuAs_2O_7$ have lower s.u. values and deviate somewhat from the values reported earlier by Wardojo & Hwu (1995) and Chen & Wang (1996). In $SrZnAs_2O_7$ and $BaCuAs_2O_7$, the alkaline earth Sr and Ba atoms occupy the $M1^{II}$ site [coordination number (CN) = 9], whereas Zn and Cu atoms occupy the $M2^{II}$ site (CN = 5). To investigate how cations of different type, size and coordination characteristics are accommodated and how $As_2O_7$ groups are adopted, we have studied the distortion of the coordination polyhedra and the conformation of the $As_2O_7$ group.

## 2. Experimental

### 2.1. Synthesis

Single crystals of both $SrZnAs_2O_7$ and $BaCuAs_2O_7$ were obtained as reaction products from the following mixtures (using an approximate 1:1:1 molar ratio in both cases) and distilled water. $SrZnAs_2O_7$ was obtained from a mixture of ZnO (Sigma–Aldrich, 99.99%), $Sr(OH)_2{\cdot}8H_2O$ (Sigma–Aldrich, 95%) and $As_2O_5$ (Alfa Products, >99.9%), and $BaCuAs_2O_7$ was obtained from a mixture of $Ba(OH)_2{\cdot}8H_2O$ (Fluka, >97%), $Cu(NO_3)_2{\cdot}H_2O$ (Sigma–Aldrich, >98%) and $As_2O_3$ (Alfa Aesar, >99.9%). The initial pH of both mixtures was 3. The Teflon vessels were enclosed in stainless steel autoclaves and both mixtures were heated under autogenous pressure. The first mixture was heated from room temperature to 493 K over a period of 4 h, held at that temperature for 72 h and cooled slowly to room temperature over a period of 72 h. The second mixture was heated from room temperature to 473 K over a period of 4 h, held at that temperature for 52 h and cooled slowly to room temperature over a period of 152 h.

**Table 2**
Experimental details.

| | $SrZnAs_2O_7$ | $BaCuAs_2O_7$ |
|---|---|---|
| Crystal data | | |
| Chemical formula | $SrZnAs_2O_7$ | $BaCuAs_2O_7$ |
| $M_r$ | 414.85 | 462.72 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 298 | 298 |
| $a, b, c$ (Å) | 5.5114 (11), 8.3524 (17), 13.106 (3) | 5.7343 (11), 8.4722 (17), 13.071 (3) |
| $\beta$ (°) | 91.01 (3) | 91.12 (3) |
| $V$ (Å$^3$) | 603.2 (2) | 634.9 (2) |
| $Z$ | 4 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 23.69 | 19.84 |
| Crystal size (mm) | 0.16 × 0.03 × 0.02 | 0.06 × 0.03 × 0.02 |
| Data collection | | |
| Diffractometer | Nonius KappaCCD diffractometer | Nonius KappaCCD diffractometer |
| Absorption correction | Multi-scan (Otwinowski & Minor, 1997) | Multi-scan (Otwinowski & Minor, 1997) |
| $T_{min}$, $T_{max}$ | 0.668, 1.000 | 0.807, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 7055, 1835, 1555 | 4991, 1298, 1232 |
| $R_{int}$ | 0.062 | 0.025 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.714 | 0.625 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.032, 0.074, 1.04 | 0.025, 0.059, 1.20 |
| No. of reflections | 1834 | 1297 |
| No. of parameters | 100 | 101 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.35, −1.20 | 2.28, −0.72 |

Computer programs: *COLLECT* (Nonius, 2002), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO-SMN* (Otwinowski *et al.*, 2003), *SIR97* (Altomare *et al.*, 1999), *SHELXL2013* (Sheldrick, 2015), *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2009), *ATOMS* (Dowty, 2000) and *publCIF* (Westrip, 2010).

At the end of the reaction, the pH of the first solvent was not measured because the sample was dry, while the pH of the second solvent was again 3. All reaction products were filtered off, washed thoroughly with distilled water and dried in air. $SrZnAs_2O_7$ crystallized as colourless elongated prismatic crystals (yield *ca* 45%) up to 0.18 mm in length, together with prisms of $Sr(AsO_3OH)$ (Mihajlović & Effenberger, 2006) (yield *ca* 40%) and undissolved ZnO powder. $BaCuAs_2O_7$ crystallized as prismatic blue–green crystals (yield *ca* 50%) up to 0.08 mm in length, together with a new Ba–Cu arsenate (yield 50%) (results to be published elsewhere).

## 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Selected bond distances and angles are listed in Tables 3 and 4 for $SrZnAs_2O_7$ and $BaCuAs_2O_7$, respectively.

## 3. Results and discussion

The unit-cell parameters of known isostructural diphosphates and diarsenates with the general formula $M1^{II}M2^{II}X_2O_7$ ($M1^{II}$ = Ca, Sr, Ba, Pb; $M2^{II}$ = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd; $X^V$ = P, As) are given in Table 1. Generally, the increase of the unit-cell volume directly follows the increase of the ionic radii of the divalent $M1$ and $M2$ cations. The unit-cell volumes for diarsenates are in the range 592.0 (2)–647.1 (2) Å$^3$, while they are smaller than 592 Å$^3$ for diphosphates, except for $SrCdP_2O_7$, $Sr_{1.34}Pb_{0.66}P_2O_7$, $BaMgP_2O_7$ and $BaMnP_2O_7$. It should be noted that the $M2^{II}$ ionic radii (0.65–0.68 Å) for diarsenates listed in Table 1 have very similar values, while the $M1^{II}$ ionic radii for CN = 9 are 1.31, 1.35 and 1.47 Å for Sr, Pb and Ba, respectively. This indicates that the unit-cell volumes for known $M1^{II}M2^{II}As_2O_7$ compounds depend mainly on the size of the $M1^{II}$ ionic radii. Earlier studies (Maass & Glaum, 2000) have shown that the unit-cell parameters of the series of diphosphates $SrM2P_2O_7$ ($M2$ = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) are dependent on the size of the $M2$ cation too. It was also found (Brown & Calvo, 1970; Alaoui El Belghiti *et al.*, 1991; Chen & Wang, 1996; Yuan *et al.*, 2007) that there is no strong correlation between the $M1$ and $M2$ cation sizes and the structure type of the $M1^{II}M2^{II}As_2O_7$ diarsenates, as was found in the corresponding diphosphates. This is because the $As_2O_7$ group is adjustable to the bonding requirements of other groups in the structure by tetrahedral distortion, by changing the $As—O_b—As$ angle as well as the dihedral angles $O_t—As1\cdots As2—O_t$ between the two $AsO_4$ tetrahedra (Chen & Wang, 1996).

The tetrahedral distortion can be expressed numerically *via* the quadratic elongation, $\lambda$, and the tetrahedral angle variances, $\sigma^2_{tet}$ (Robinson *et al.*, 1971); the values were calculated using the *VOLCAL* program (Hazen & Finger, 1982) as implemented in *WinGX* (Farrugia, 2012). Since the bridging ($O_b$) and six terminal ($O_t$) O atoms of the $As_2O_7$ group of $M1^{II}M2^{II}As_2O_7$ are located in general positions, three symmetrically independent dihedral or torsion angles can be distinguished within the group. Similar to tetrahedral angle

**Table 3**
Selected geometric parameters (Å, °) for $SrZnAs_2O_7$.

| | | | |
|---|---|---|---|
| Sr1—O2 | 2.525 (3) | As1—O1$^{iii}$ | 1.671 (3) |
| Sr1—O1$^{i}$ | 2.557 (3) | As1—O4 | 1.744 (3) |
| Sr1—O2$^{ii}$ | 2.576 (3) | As2—O5$^{v}$ | 1.669 (3) |
| Sr1—O6$^{iii}$ | 2.602 (3) | As2—O7$^{iv}$ | 1.679 (3) |
| Sr1—O3$^{ii}$ | 2.640 (3) | As2—O6 | 1.682 (3) |
| Sr1—O7$^{iv}$ | 2.714 (3) | As2—O4$^{ii}$ | 1.749 (3) |
| Sr1—O5$^{i}$ | 2.765 (3) | Zn1—O3 | 1.973 (3) |
| Sr1—O1$^{iii}$ | 2.851 (3) | Zn1—O5 | 2.013 (3) |
| Sr1—O5$^{iii}$ | 3.268 (3) | Zn1—O6 | 2.023 (3) |
| As1—O2$^{iii}$ | 1.654 (3) | Zn1—O7 | 2.106 (3) |
| As1—O3$^{ii}$ | 1.670 (3) | Zn1—O1 | 2.157 (3) |
| | | | |
| O2—Sr1—O1$^{i}$ | 93.44 (10) | O2$^{ii}$—Sr1—O5$^{iii}$ | 139.81 (9) |
| O2—Sr1—O2$^{ii}$ | 155.50 (7) | O6$^{iii}$—Sr1—O5$^{iii}$ | 61.41 (9) |
| O1$^{i}$—Sr1—O2$^{ii}$ | 69.30 (10) | O3$^{ii}$—Sr1—O5$^{iii}$ | 106.87 (9) |
| O2—Sr1—O6$^{iii}$ | 120.91 (10) | O7$^{iv}$—Sr1—O5$^{iii}$ | 60.98 (9) |
| O1$^{i}$—Sr1—O6$^{iii}$ | 140.59 (10) | O5$^{i}$—Sr1—O5$^{iii}$ | 146.28 (9) |
| O2$^{ii}$—Sr1—O6$^{iii}$ | 81.88 (10) | O1$^{iii}$—Sr1—O5$^{iii}$ | 50.28 (8) |
| O2—Sr1—O3$^{ii}$ | 99.39 (10) | O2$^{iii}$—As1—O3$^{ii}$ | 114.79 (16) |
| O1$^{i}$—Sr1—O3$^{ii}$ | 120.53 (10) | O2$^{iii}$—As1—O1$^{iii}$ | 113.26 (16) |
| O2$^{ii}$—Sr1—O3$^{ii}$ | 76.47 (10) | O3$^{ii}$—As1—O1$^{iii}$ | 106.36 (16) |
| O6$^{iii}$—Sr1—O3$^{ii}$ | 75.40 (10) | O2$^{iii}$—As1—O4 | 108.51 (17) |
| O2—Sr1—O7$^{iv}$ | 98.52 (11) | O3$^{ii}$—As1—O4 | 105.51 (16) |
| O1$^{i}$—Sr1—O7$^{iv}$ | 81.41 (10) | O1$^{iii}$—As1—O4 | 107.95 (15) |
| O2$^{ii}$—Sr1—O7$^{iv}$ | 95.96 (10) | O5$^{v}$—As2—O7$^{iv}$ | 118.74 (15) |
| O6$^{iii}$—Sr1—O7$^{iv}$ | 75.32 (9) | O5$^{v}$—As2—O6 | 111.75 (16) |
| O3$^{ii}$—Sr1—O7$^{iv}$ | 150.51 (10) | O7$^{iv}$—As2—O6 | 109.62 (15) |
| O2—Sr1—O5$^{i}$ | 83.80 (10) | O5$^{v}$—As2—O4$^{ii}$ | 101.56 (15) |
| O1$^{i}$—Sr1—O5$^{i}$ | 59.01 (10) | O7$^{iv}$—As2—O4$^{ii}$ | 108.69 (15) |
| O2$^{ii}$—Sr1—O5$^{i}$ | 72.49 (10) | O6—As2—O4$^{ii}$ | 105.33 (15) |
| O6$^{iii}$—Sr1—O5$^{i}$ | 136.65 (10) | O3—Zn1—O5 | 116.04 (13) |
| O3$^{ii}$—Sr1—O5$^{i}$ | 65.08 (9) | O3—Zn1—O6 | 142.82 (13) |
| O7$^{iv}$—Sr1—O5$^{i}$ | 140.40 (9) | O5—Zn1—O6 | 98.26 (13) |
| O2—Sr1—O1$^{iii}$ | 65.43 (9) | O3—Zn1—O7 | 85.04 (13) |
| O1$^{i}$—Sr1—O1$^{iii}$ | 156.84 (6) | O5—Zn1—O7 | 118.29 (12) |
| O2$^{ii}$—Sr1—O1$^{iii}$ | 127.02 (9) | O6—Zn1—O7 | 91.26 (12) |
| O6$^{iii}$—Sr1—O1$^{iii}$ | 62.52 (9) | O3—Zn1—O1 | 87.94 (13) |
| O3$^{ii}$—Sr1—O1$^{iii}$ | 58.16 (9) | O5—Zn1—O1 | 78.02 (12) |
| O7$^{iv}$—Sr1—O1$^{iii}$ | 109.88 (9) | O6—Zn1—O1 | 85.46 (12) |
| O5$^{i}$—Sr1—O1$^{iii}$ | 106.95 (9) | O7—Zn1—O1 | 163.69 (12) |
| O2—Sr1—O5$^{iii}$ | 64.66 (10) | As1—O4—As2$^{vi}$ | 122.39 (18) |
| O1$^{i}$—Sr1—O5$^{iii}$ | 130.69 (9) | | |

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

variances, $\sigma^2_{\rm tet}$ [$= \Sigma(\theta_i - 109.47)^2/5$, $i = 1, 2, 3, 4, 5, 6$], the formula $\sigma^2_{\rm dih} = \Sigma(\theta_i - 60)^2/3$ ($i = 1, 2, 3$) was used to calculate the dihedral angle variances and the dihedral angles were calculated using the program *PLATON* (Spek, 2009). Diarsenate groups in $M1^{\rm II}M2^{\rm II}As_2O_7$ compounds involve two crystallographically non-equivalent $AsO_4$ tetrahedra (Fig. 1). In the structures of $SrZnAs_2O_7$ and $BaCuAs_2O_7$, nearly identical average ⟨As1—O⟩ bond lengths were found (Table 5). The mean ⟨As2—O⟩ distances in $SrZnAs_2O_7$ and $BaCuAs_2O_7$ are also almost identical and longer than the corresponding values for ⟨As1—O⟩, which correlate with the distinct angular distortions in the As1O$_4$ ($\sigma^2_{\rm tet}$ = 14.24 and 14.96) and As2O$_4$ ($\sigma^2_{\rm tet}$ = 34.26 and 34.80) tetrahedra (Table 5 and Fig. 2). The longest As—O bonds are to the bridging O4 atom. The As1—O4—As2 bond angles are 122.39 (18) and 125.3 (2)° in $SrZnAs_2O_7$ and $BaCuAs_2O_7$, respectively, which compare well with the same bridging angles of 122.7 (3)° in $SrCoAs_2O_7$ (Horng & Wang, 1994), 122.7 (3)° in $SrCuAs_2O_7$ (Chen & Wang, 1996), as well as values of 125.9 (3) (Wardojo & Hwu, 1995) and 124.7 (6)° (Chen & Wang, 1996) in two different forms of $BaCuAs_2O_7$. In $SrZnAs_2O_7$ and $BaCuAs_2O_7$, two $AsO_4$ tetrahedra of the diarsenate group form a staggered conformation [dihedral angles O1—As1···As2—O7, O2—As1···As2—O6 and O3—As1···As2—O5 of 36.50 (15), 40.93 (16) and 69.86 (19)°, respectively, for $SrZnAs_2O_7$, and 42.7 (2), 48.1 (2) and 74.0 (3)°, respectively, for $BaCuAs_2O_7$]. The dihedral angle variances, $\sigma^2_{\rm dih}$, are 337.71 and 212.30 for $SrZnAs_2O_7$ and $BaCuAs_2O_7$, respectively. This points to a greater $As_2O_7$ angular deviation from the ideal value of 60° in $SrZnAs_2O_7$ than in $BaCuAs_2O_7$ (Table 5 and Fig. 2).

Each diarsenate group shares its five corners with five different $M2O_5$ square pyramids. This leaves one corner free (O2 in $SrZnAs_2O_7$ and $BaCuAs_2O_7$) and this participates in the coordination of the $M1^{\rm II}$ cation. The $M2$ position is characterized by a square-pyramidal geometry and a 4 + 1 bond

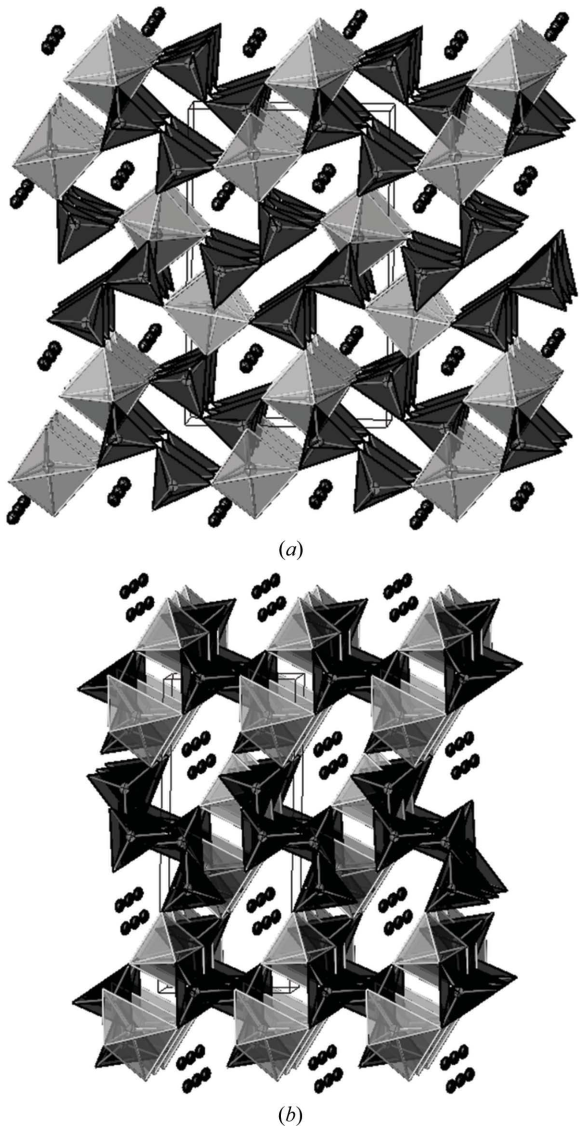


**Figure 1**
Polyhedral views of the framework in the $SrZnAs_2O_7$ structure (*a*) along the [100] direction (the *c* axis is vertical) and (*b*) along the [010] direction (the *c* axis is vertical). A trace of the unit cell is drawn for reference. $AsO_4$ tetrahedra are dark grey, $ZnO_5$ pyramids are light grey and Sr atoms are represented by black spheres.

distance scheme. The average lengths of the four basal $M2$—O bonds are 2.029 (3) and 1.977 (4) Å, and the fifth axial bond is longer, *i.e.* 2.157 (3) and 2.382 (4) Å, for $SrZnAs_2O_7$ and $BaCuAs_2O_7$, respectively. The mean ⟨Zn—O⟩ and ⟨Cu—O⟩ distances are 2.054 (3) and 2.060 (4) Å. They can be compared to the ⟨$M2$—O⟩ distances of 2.062 Å found in $BaZnAs_2O_7$ (Đorđević, 2008) and 2.035 Å found in $SrCuAs_2O_7$ (Chen & Wang, 1996). In both structures, the $M2$ atom deviates from the least-squares basal plane [0.4683 (5) and 0.2411 (7) Å for Zn and Cu, respectively] towards the axial O atom. As reported previously (Riou & Raveau, 1991; Horng & Wang, 1994; Wardojo & Hwu, 1995), the $M2$ atoms tend to be located close to the centre of the $M2O_5$ pyramid, unlike Cu atoms, which are located closer to the square basal plane, leading to a long Cu—O apical distance. This is in agreement with the Jahn–Teller effect of the $Cu^{II}$ cation.

Considering the bond distances in $SrZnAs_2O_7$ and $BaCuAs_2O_7$, the coordination of the Sr/Ba-hosting site $M1$ with CN = 9 is approximately 3 + 3 + 3 and can be described as a distorted tricapped trigonal prism. The average ⟨Sr—O⟩ and ⟨Ba—O⟩ bond distances are 2.722 (3) and 2.821 (4) Å, which compare well with the average ⟨Sr—O⟩ and ⟨Ba—O⟩ bond distances of 2.705 Å in $SrCuAs_2O_7$ (Chen & Wang, 1996) and 2.829 Å in $BaCoAs_2O_7$ (Mihajlović *et al.*, 2004). It should be noted that some authors (Pertlik, 1986; Horng & Wang, 1994) describe $M1$ as eight-coordinated, taking into account only O atoms at distances less than 3 Å. In order to observe $M1$ cations in a similar environment and to compare the distortion parameters in different diarsenates, the same CN = 9 for all $M1$ cations was assumed. The bond-valence calculations (Brown, 1996; Wills, 2010) show that the Sr atom in $SrZnAs_2O_7$ is in good agreement with its formal oxidation state ($\Sigma\nu_{ij}$ = 1.99 v.u.) if CN = 9, although the longest Sr—O bond length [3.268 (3) Å] contributes only 2% to the bond-valence sum. The sum of the bond valences of the Ba atom in $BaCuAs_2O_7$ suggests a slight oversaturation if all nine ligands are considered ($\Sigma\nu_{ij}$ = 2.2 v.u.), but it is the same as the value calculated for $BaCoAs_2O_7$ (Mihajlović *et al.*, 2004). The longest Ba—O distance [3.008 (4) Å] contributes 6% to the bond-valence sum.

**Table 4**
Selected geometric parameters (Å, °) for $BaCuAs_2O_7$.

| | | | |
|---|---|---|---|
| Ba1—O2 | 2.628 (4) | As1—O1$^{ii}$ | 1.685 (4) |
| Ba1—O2$^{i}$ | 2.683 (5) | As1—O4 | 1.744 (4) |
| Ba1—O6$^{ii}$ | 2.764 (4) | As2—O5$^{v}$ | 1.650 (4) |
| Ba1—O7$^{iii}$ | 2.803 (4) | As2—O6 | 1.685 (4) |
| Ba1—O1$^{iv}$ | 2.803 (4) | As2—O7$^{iii}$ | 1.698 (4) |
| Ba1—O3$^{i}$ | 2.850 (4) | As2—O4$^{i}$ | 1.752 (4) |
| Ba1—O5$^{iv}$ | 2.904 (4) | Cu1—O3 | 1.932 (4) |
| Ba1—O1$^{ii}$ | 2.938 (4) | Cu1—O7 | 1.976 (4) |
| Ba1—O5$^{ii}$ | 3.008 (4) | Cu1—O6 | 1.983 (4) |
| As1—O2$^{ii}$ | 1.654 (4) | Cu1—O1 | 2.025 (4) |
| As1—O3$^{i}$ | 1.663 (4) | Cu1—O5 | 2.382 (4) |
| | | | |
| O2—Ba1—O2$^{i}$ | 153.81 (10) | O6$^{ii}$—Ba1—O5$^{ii}$ | 65.41 (12) |
| O2—Ba1—O6$^{ii}$ | 125.38 (13) | O7$^{iii}$—Ba1—O5$^{ii}$ | 63.22 (12) |
| O2$^{i}$—Ba1—O6$^{ii}$ | 76.68 (13) | O1$^{iv}$—Ba1—O5$^{ii}$ | 131.40 (12) |
| O2—Ba1—O7$^{iii}$ | 104.89 (14) | O3$^{i}$—Ba1—O5$^{ii}$ | 106.90 (12) |
| O2$^{i}$—Ba1—O7$^{iii}$ | 91.88 (14) | O5$^{iv}$—Ba1—O5$^{ii}$ | 151.54 (11) |
| O6$^{ii}$—Ba1—O7$^{iii}$ | 80.15 (13) | O1$^{ii}$—Ba1—O5$^{ii}$ | 53.01 (11) |
| O2—Ba1—O1$^{iv}$ | 90.97 (13) | O2$^{ii}$—As1—O3$^{i}$ | 115.9 (2) |
| O2$^{i}$—Ba1—O1$^{iv}$ | 71.47 (13) | O2$^{ii}$—As1—O1$^{ii}$ | 112.0 (2) |
| O6$^{ii}$—Ba1—O1$^{iv}$ | 142.42 (13) | O3$^{i}$—As1—O1$^{ii}$ | 105.5 (2) |
| O7$^{iii}$—Ba1—O1$^{iv}$ | 81.45 (12) | O2$^{ii}$—As1—O4 | 108.5 (2) |
| O2—Ba1—O3$^{i}$ | 96.66 (13) | O3$^{i}$—As1—O4 | 106.6 (2) |
| O2$^{i}$—Ba1—O3$^{i}$ | 76.64 (13) | O1$^{ii}$—As1—O4 | 108.0 (2) |
| O6$^{ii}$—Ba1—O3$^{i}$ | 70.14 (13) | O5$^{v}$—As2—O6 | 115.4 (2) |
| O7$^{iii}$—Ba1—O3$^{i}$ | 149.83 (13) | O5$^{v}$—As2—O7$^{iii}$ | 117.7 (2) |
| O1$^{iv}$—Ba1—O3$^{i}$ | 119.53 (12) | O6—As2—O7$^{iii}$ | 108.5 (2) |
| O2—Ba1—O5$^{iv}$ | 83.98 (14) | O5$^{v}$—As2—O4$^{i}$ | 104.0 (2) |
| O2$^{i}$—Ba1—O5$^{iv}$ | 70.11 (13) | O6—As2—O4$^{i}$ | 104.5 (2) |
| O6$^{ii}$—Ba1—O5$^{iv}$ | 129.47 (13) | O7$^{iii}$—As2—O4$^{i}$ | 105.4 (2) |
| O7$^{iii}$—Ba1—O5$^{iv}$ | 136.35 (12) | O3—Cu1—O7 | 87.90 (19) |
| O1$^{iv}$—Ba1—O5$^{iv}$ | 55.40 (12) | O3—Cu1—O6 | 158.73 (19) |
| O3$^{i}$—Ba1—O5$^{iv}$ | 65.93 (12) | O7—Cu1—O6 | 89.01 (18) |
| O2—Ba1—O1$^{ii}$ | 70.08 (13) | O3—Cu1—O1 | 91.48 (18) |
| O2$^{i}$—Ba1—O1$^{ii}$ | 121.67 (12) | O7—Cu1—O1 | 172.97 (17) |
| O6$^{ii}$—Ba1—O1$^{ii}$ | 58.97 (12) | O6—Cu1—O1 | 89.03 (18) |
| O7$^{iii}$—Ba1—O1$^{ii}$ | 113.44 (12) | O3—Cu1—O5 | 109.54 (17) |
| O1$^{iv}$—Ba1—O1$^{ii}$ | 158.02 (6) | O7—Cu1—O5 | 113.23 (17) |
| O3$^{i}$—Ba1—O1$^{ii}$ | 54.80 (12) | O6—Cu1—O5 | 90.99 (17) |
| O5$^{iv}$—Ba1—O1$^{ii}$ | 109.76 (12) | O1—Cu1—O5 | 73.56 (16) |
| O2—Ba1—O5$^{ii}$ | 69.15 (13) | As1—O4—As2$^{vi}$ | 125.3 (2) |
| O2$^{i}$—Ba1—O5$^{ii}$ | 137.03 (13) | | |

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

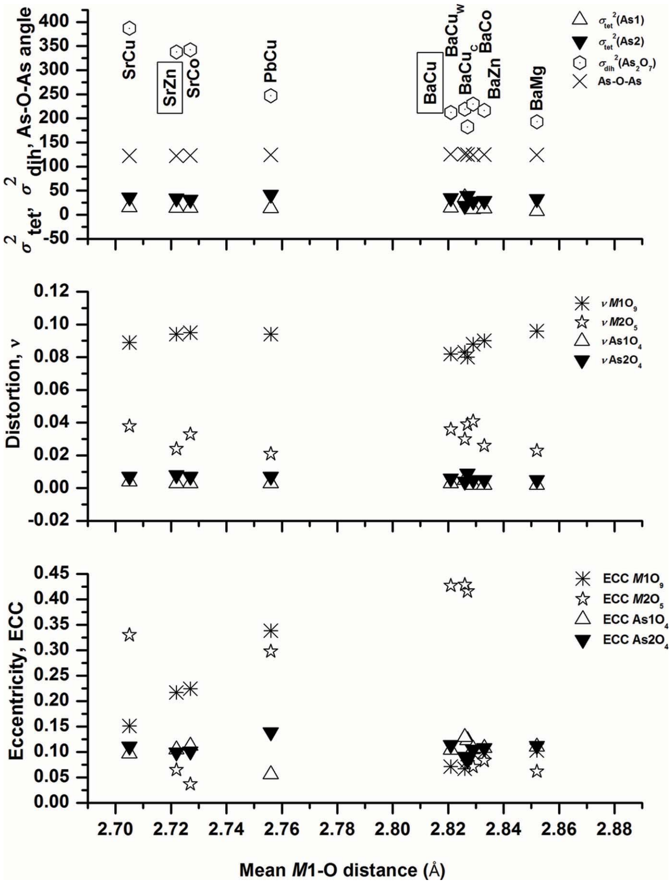


**Figure 2**
Distortion parameters *versus* average ⟨$M1$—O⟩ distances in $M1^{II}M2^{II}As_2O_7$ ($M1^{II}$ = Sr, Ba, Pb; $M2^{II}$ = Mg, Co, Cu, Zn) compounds. Framed symbols are for $SrZnAs_2O_7$ and $BaCuAs_2O_7$.

As a measure for polyhedron distortion of the $AsO_4$ tetrahedra, the $M1O_9$ tricapped trigonal prisms and the $M2O_5$ square pyramids, the volume-based eccentricity (ECC) and

**Table 5**
Geometrical characteristics of the coordination polyhedra for $M1^{II}M2^{II}As_2O_7$ compounds ($M1$ = $Ba^{2+}$, $Sr^{2+}$, $Pb^{2+}$,$Ca^{2+}$, $M2$ = $Cu^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cr^{2+}$).

| Compound | Central atom (CN) | Average $M$—O bond distance (Å) | Radius of a fitted circumscribed sphere (Å) | Sum of ionic radii for the bonds* (Å) | Volume-based ECCs | Volume-based distortion, $\nu$ | $\sigma^2_{tet}$, λ(As1), $\sigma^2_{tet}$, λ(As2), As1—$O_b$—As2 angle (°), $\sigma^2_{dih}$# |
|---|---|---|---|---|---|---|---|
| $SrCuAs_2O_7$[1] | As1 (4) | 1.683±0.037 | 1.683 | 1.715 | 0.097 | 0.004 | 15.73, 1.0038 |
| | As2 (4) | 1.695±0.041 | 1.692 | 1.715 | 0.111 | 0.007 | 35.89, 1.0089 |
| | Sr (9) | 2.705±0.175 | 2.699 | 2.69 | 0.151 | 0.089 | 122 (2) |
| | Cu (5) | 2.035±0.133 | 2.026 | 2.03 | 0.330 | 0.038 | 386.89 |
| $SrCoAs_2O_7$[2] | As1 (4) | 1.682±0.043 | 1.680 | 1.715 | 0.112 | 0.003 | 14.25, 1.0035 |
| | As2 (4) | 1.693±0.037 | 1.691 | 1.715 | 0.101 | 0.007 | 31.73, 1.0078 |
| | Sr (9) | 2.727±0.235 | 2.718 | 2.69 | 0.224 | 0.095 | 122.7 (3) |
| | Co (5) | 2.063±0.068 | 2.061 | 2.05 | 0.037 | 0.033 | 342.20 |
| $SrZnAs_2O_7$[3] | As1 (4) | 1.685±0.040 | 1.684 | 1.715 | 0.105 | 0.003 | 14.24, 1.0032 |
| | As2 (4) | 1.695±0.037 | 1.692 | 1.715 | 0.099 | 0.008 | 34.26, 1.0085 |
| | Sr (9) | 2.722±0.231 | 2.714 | 2.69 | 0.217 | 0.094 | 122.39 (18) |
| | Zn (5) | 2.054±0.075 | 2.053 | 2.06 | 0.065 | 0.024 | 337.71 |
| $PbCuAs_2O_7$[4] | As1 (4) | 1.686±0.021 | 1.686 | 1.715 | 0.056 | 0.003 | 13.77, 1.0033 |
| | As2 (4) | 1.701±0.052 | 1.697 | 1.715 | 0.139 | 0.007 | 41.62, 1.0103 |
| | Pb (9) | 2.756±0.278 | 2.744 | 2.73 | 0.338 | 0.094 | 124.46 (8) |
| | Cu (5) | 2.033±0.121 | 2.023 | 2.03 | 0.298 | 0.021 | 246.99 |
| $BaCuAs_2O_7$[1] | As1 (4) | 1.690±0.047 | 1.688 | 1.715 | 0.123 | 0.005 | 25.04, 1.0037 |
| | As2 (4) | 1.695±0.031 | 1.692 | 1.715 | 0.084 | 0.009 | 39.06, 1.0095 |
| | Ba (9) | 2.827±0.126 | 2.820 | 2.85 | 0.083 | 0.080 | 123 (3) |
| | Cu (5) | 2.047±0.175 | 2.038 | 2.03 | 0.416 | 0.039 | 182.37 |
| $BaCuAs_2O_7$[3] | As1 (4) | 1.686±0.039 | 1.685 | 1.715 | 0.104 | 0.003 | 14.96, 1.0039 |
| | As2 (4) | 1.696±0.042 | 1.693 | 1.715 | 0.114 | 0.006 | 34.80, 1.0082 |
| | Ba (9) | 2.821±0.120 | 2.816 | 2.85 | 0.071 | 0.082 | 125.32 (19) |
| | Cu (5) | 2.057±0.183 | 2.049 | 2.03 | 0.427 | 0.036 | 212.30 |
| $BaCuAs_2O_7$[5] | As1 (4) | 1.695±0.049 | 1.691 | 1.715 | 0.129 | 0.005 | 36.04, 1.0087 |
| | As2 (4) | 1.682±0.035 | 1.681 | 1.715 | 0.091 | 0.004 | 18.57, 1.0033 |
| | Ba (9) | 2.826±0.120 | 2.822 | 2.85 | 0.067 | 0.083 | 125.9 (3) |
| | Cu (5) | 2.061±0.185 | 2.053 | 2.03 | 0.429 | 0.030 | 219.00 |
| $BaMgAs_2O_7$[6] | As1 (4) | 1.685±0.042 | 1.685 | 1.715 | 0.110 | 0.002 | 7.96, 1.0022 |
| | As2 (4) | 1.694±0.042 | 1.692 | 1.715 | 0.112 | 0.005 | 32.70, 1.0069 |
| | Ba (9) | 2.852±0.178 | 2.848 | 2.85 | 0.103 | 0.096 | 125.0 (2) |
| | Mg (5) | 2.049±0.038 | 2.047 | 2.04 | 0.062 | 0.023 | 192.99 |
| $BaCoAs_2O_7$[6] | As1 (4) | 1.686±0.041 | 1.685 | 1.715 | 0.106 | 0.002 | 11.91, 1.003 |
| | As2 (4) | 1.696±0.039 | 1.693 | 1.715 | 0.105 | 0.005 | 27.55, 1.007 |
| | Ba (9) | 2.829±0.154 | 2.824 | 2.85 | 0.097 | 0.088 | 125.0 (2) |
| | Co (5) | 2.069±0.056 | 2.066 | 2.05 | 0.071 | 0.041 | 229.64 |
| $BaZnAs_2O_7$[7] | As1 (4) | 1.687±0.041 | 1.686 | 1.715 | 0.108 | 0.002 | 12.71, 1.0028 |
| | As2 (4) | 1.690±0.040 | 1.688 | 1.715 | 0.108 | 0.005 | 28.97, 1.0073 |
| | Ba (9) | 2.833±0.164 | 2.829 | 2.85 | 0.100 | 0.090 | 124.67 (14) |
| | Zn (5) | 2.061±0.054 | 2.059 | 2.06 | 0.083 | 0.026 | 216.59 |

Notes: (*) calculated from effective ionic radii (Shannon, 1976); (#) $\sigma^2_{dih} = \Sigma(\theta_i - 60)^2/3$ ($i = 1, 2, 3$). References: (**1**) Chen & Wang (1996); (**2**) Horng & Wang (1994); (**3**) this work; (**4**) Pertlik (1986); (**5**) Wardojo & Hwu (1995); (**6**) Mihajlović *et al.* (2004); (**7**) Đorđević (2008).

the volume-based distortion ($\nu$) were calculated using the program *IVTON* (Balić-Žunić & Makovicky, 1996; Makovicky & Balić-Žunić, 1998). The ECC is a measure of the displacement of the central atom from the centroid of the coordination polyhedron defined as the point for which the variance of squares of the central cation-to-corner ligand distances is at a minimum. The $\nu$ parameter is an overall measure of polyhedral distortion which can be defined as the regularity of distribution of the ligand atoms irrespective of the position of the central atom in the polyhedron. Unsurprisingly, in all the $M1^{II}M2^{II}As_2O_7$ compounds, the $As1O_4$ and $As2O_4$ tetrahedra are less distorted than the $M1O_9$ and $M2O_5$ polyhedra. The mean quadratic elongation, λ, and the tetrahedral angle variance, $\sigma^2_{tet}$, indicate that the $As2O_4$ tetrahedra are a little more distorted than $As1O_4$ (Table 5 and Fig. 2). The low ECC (0.056–0.123 for $As1O_4$ and 0.084–0.139 for $As2O_4$) and low $\nu$ (0.002–0.005 for $As1O_4$ and 0.004–0.009 for $As2O_4$) reflect the regularity of the tetrahedra (Fig. 2). The bridging bond angles

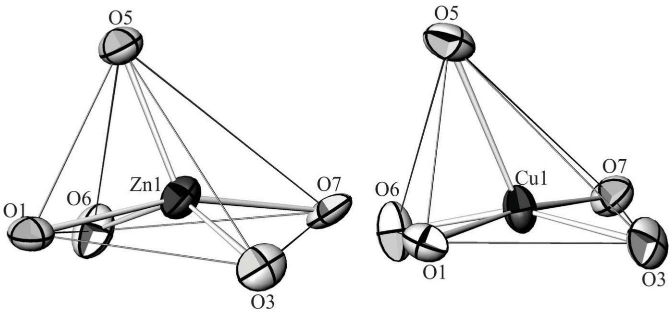


**Figure 3**
Displacement ellipsoid plot (90% probability level) of the $M2O_5$ square pyramids in $SrZnAs_2O_7$ and $BaCuAs_2O_7$, showing the distortion and the atomic numbering schemes.

As1—O$_b$—As2 range from 122.4 (2) to 125.3 (2)° and depend slightly on the $M1$ cation size (Table 5), *i.e.* the angles become a little wider as the $M1$ cation becomes larger. In contrast, the values of the dihedral angle variances depend greatly on the $M1$ cation size and the variance becomes smaller as the $M1$ cations become larger, suggesting that a smaller $M1$ cation causes a larger dihedral angle deviation from the ideal value of 60°. The ECC (0.037–0.083) of the $M2^{\rm II}$ cations in the $ZnO_5$, $CoO_5$ and $MgO_5$ pyramids are low, indicating that these $M2^{\rm II}$ cations are located close to the centroid of the $M2O_5$ pyramids. The ECC (0.298–0.429) clearly increases with the incorporation of Cu$^{\rm II}$ cations in the $M2$ position (Table 5 and Fig. 2) leading to the almost uniform Cu—O basal distances and a longer Cu—O apical distance, which is in agreement with the Jahn–Teller effect of the Cu$^{\rm II}$ cation (Fig. 3). The $M2$ sites in three $BaCuAs_2O_7$ compounds have the highest eccentricity of all. $PbCuAs_2O_7$ displays a more eccentric $Pb1O_9$ polyhedron than the Sr- and Ba-containing $M1^{\rm II}M2^{\rm II}As_2O_7$ compounds, because of its inert electron pair. The $\nu$ values (0.021–0.041) of the $M2O_5$ polyhedra are, as expected, higher than for the $As1O_4$ and $As2O_4$ tetrahedra, but lower than for the $M1O_9$ coordination polyhedra: $\nu(BaO_9) = 0.080 - 0.096$ ($\langle 0.082 \rangle$), $\nu(SrO_9) = 0.089 - 0.095$ ($\langle 0.094 \rangle$) and $\nu(PbO_9) = 0.094$ (Table 5). These values indicate a slightly lower distortion of the $M1O_9$ coordination polyhedra for larger $M1^{\rm II}$ cations. It is interesting that $\nu$ has the largest values in compounds containing Co, *i.e.* for the $CoO_5$ pyramid in $BaCoAs_2O_7$ and for the $SrO_9$ polyhedra in $SrCoAs_2O_7$. In $SrZnAs_2O_7$ and $BaCuAs_2O_7$, although both $M1^{\rm II}$ cations are moved from the corresponding centroids [ECC(Sr) = 0.217 and ECC(Ba) = 0.071], judging by the $\nu$ values [$\nu$(Sr) = 0.094 and $\nu$(Ba) = 0.082], the coordinated O atoms form quite regular polyhedra.

As already mentioned, the lattice parameters obtained for $BaCuAs_2O_7$ deviate somewhat from the values reported earlier by Wardojo & Hwu (1995) and Chen & Wang (1996). The slight increase in unit-cell volume of approximately 4 Å$^3$ [632.7 (2), 634.9 (2) and 636.6 (6) Å$^3$ for BaCu$_{\rm C}$, BaCu and BaCu$_{\rm W}$, respectively; Table 5 and Fig. 2] reflects the increase of the dihedral angle variances, $\sigma^2_{\rm dih}$, which are 182.37, 212.30 and 219.00° for BaCu$_{\rm C}$, BaCu and BaCu$_{\rm W}$, respectively. This indicates that the smallest $As_2O_7$ angular deviation in $BaCuAs_2O_7$ corresponds to the smallest unit cell (Table 5 and Fig. 2). Contrary to the dihedral angle variances, the tetrahedral angle variances, $\sigma^2_{\rm tet}$, vary over relatively small intervals, *viz.* 14.96–25.04 and 34.80–39.06°, which confirms the statement that the $As_2O_7$ group is adjustable with regard to the bonding requirements. The other geometrical characteristics of the coordination polyhedra are nearly the same.

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## References

Adams, R. D., Layland, R. C. & Payen, C. (1995). *Polyhedron*, **14**, 3473–3480.
Alaoui El Belghiti, A., Boukhari, A. & Holt, E. M. (1991). *Acta Cryst.* C**47**, 473–477.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Balić-Žunić, T. & Makovicky, E. (1996). *Acta Cryst.* B**52**, 78–81.
Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.
Brown, I. D. & Calvo, C. (1970). *J. Solid State Chem.* **1**, 173–179.
Calvo, C. (1968). *Inorg. Chem.* **7**, 1345–1351.
Chen, T. C. & Wang, S. L. (1996). *J. Solid State Chem.* **121**, 350–355.
Đorđević, T. (2008). *Acta Cryst.* E**64**, i57.
Dowty, E. (2000). *ATOMS for Windows*. Shape Software, Kingsport, Tennessee, USA.
Edhokkar, F., Hadrich, A., Graia, M. & Mhiri, T. (2012). *2012 IOP Conf. Ser. Mater. Sci. Eng.* **28**, 012017.
El Bali, B., Boukhari, A., Aride, J., Maass, K., Wald, D., Glaum, R. & Abraham, F. (2001). *Solid State Sci.* **3**, 669–676.
Elmarzouki, A., Boukhari, A., Holt, E. M. & Berrada, A. (1994). *J. Alloys Compd*, **204**, 127–131.
Elmarzouki, A., Boukhari, A., Holt, E. M. & Berrada, A. (1995). *J. Alloys Compd*, **227**, 125–130.
Faggiani, R. & Calvo, C. (1976). *Can. J. Chem.* **54**, 3319–3324.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Hazen, R. M. & Finger, L. W. (1982). In *Comparative Crystal Chemistry*, p. 86 and Appendix III. Chichester: Wiley.
Höppe, H. A., Daub, M. & Bröhmer, M. C. (2007). *Chem. Mater.* **19**, 6358–6362.
Horchani-Naifer, K. & Férid, M. (2007). *Acta Cryst.* E**63**, i33–i34.
Horng, J.-C. & Wang, S.-L. (1994). *Acta Cryst.* C**50**, 488–490.
ICSD (2014). Inorganic Crystal Structure Database. FIZ-Karlsruhe, Germany. http://icsd.fiz-karlsruhe.de/icsd/.
Kolitsch, U. (2004). *Z. Kristallogr. New Cryst. Struct.* **219**, 207–208.
Le Meins, J.-M. & Courbion, G. (1999). *Acta Cryst.* C**55**, 481–483.
Maass, K. & Glaum, R. (2000). *Acta Cryst.* C**56**, 404–406.
Makovicky, E. & Balić-Žunić, T. (1998). *Acta Cryst.* B**54**, 766–773.
Marzouki, R., Guesmi, A., Zid, M. F. & Driss, A. (2012). *Cryst. Struct. Theor. Appl.* **1**, 68–73.
Mihajlović, T. & Effenberger, H. (2006). *Z. Kristallogr.* **221**, 770–781.
Mihajlović, T., Kolitsch, U. & Effenberger, H. (2004). *J. Alloys Compd*, **379**, 103–109.
Moqine, A., Boukhari, A., Elammari, L. & Durand, J. (1993). *J. Solid State Chem.* **107**, 368–372.
Murashova, E. V., Velikodnyi, Y. A. & Trunov, V. K. (1991). *Zh. Neorg. Khim.* **36**, 851–854.
Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z., Borek, D., Majewski, W. & Minor, W. (2003). *Acta Cryst.* A**59**, 228–234.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Ouerfelli, N., Guesmi, A., Molinié, P., Mazza, D., Zid, M. F. & Driss, A. (2007). *J. Solid State Chem.* **180**, 2942–2949.
Pertlik, F. (1986). *Monatsh. Chem.* **117**, 1343–1348.
Riou, D. & Goreaud, M. (1990). *Acta Cryst.* C**46**, 1191–1193.
Riou, D. & Raveau, B. (1991). *Acta Cryst.* C**47**, 1708–1709.
Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.
Rousse, G., Rodríguez-Carvajal, J., Wurm, C. & Masquelier, C. (2013). *Phys. Rev. B*, **88**, 214433.
Schwendtner, K. & Kolitsch, U. (2004). *Acta Cryst.* C**60**, i79–i83.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Tahiri, A. A., Bali, B. E., Lachkar, M., Ouarsal, R. & Zavalij, P. Y. (2002). *Acta Cryst.* E**58**, i9–i11.

Wardojo, T. A. & Hwu, S. J. (1995). *J. Solid State Chem.* **118**, 280–284.

Weil, M., Đorđević, T., Lengauer, C. L. & Kolitsch, U. (2009). *Solid State Sci.* **11**, 2111–2117.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Wills, A. S. (2010). *VaList*. http://www.CCP14.ac.uk.

Yuan, J. L., Zeng, X. Y., Zhao, J. T., Zhang, Z. J., Chen, H. H. & Zhang, G. B. (2007). *J. Solid State Chem.* **180**, 3310–3316.

# supporting information

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# An investigation of polyhedral deformation in two mixed-metal diarsenates: $SrZnAs_2O_7$ and $BaCuAs_2O_7$

**Sabina Kovač, Ljiljana Karanović and Tamara Đorđević**

## Computing details

For both compounds, data collection: *COLLECT* (Nonius, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009) for SrZnAs2O7; *SHELXL2013* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012) for BaCuAs2O7. For both compounds, molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## (SrZnAs2O7) Strontium zinc diarsenic heptaoxide

*Crystal data*

$SrZnAs_2O_7$
$M_r = 414.85$
Monoclinic, $P2_1/n$
$a = 5.5114$ (11) Å
$b = 8.3524$ (17) Å
$c = 13.106$ (3) Å
$\beta = 91.01$ (3)°
$V = 603.2$ (2) Å$^3$
$Z = 4$
$F(000) = 760$
$D_x = 4.568$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\mu = 23.69$ mm$^{-1}$
$T = 298$ K
Prismatic, blue-green
0.16 × 0.03 × 0.02 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed X-ray tube
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (Otwinowski & Minor, 1997)
$T_{min} = 0.668$, $T_{max} = 1.000$
7055 measured reflections
1835 independent reflections
1555 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$
$\theta_{max} = 30.5°$, $\theta_{min} = 2.9°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.074$
$S = 1.04$
1834 reflections
100 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 1.0702P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.35$ e Å$^{-3}$
$\Delta\rho_{min} = -1.20$ e Å$^{-3}$

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{\rm iso}$*/$U_{\rm eq}$ |
|---|---|---|---|---|
| Sr1 | 0.20949 (7) | 0.67034 (5) | 0.21859 (3) | 0.01119 (11) |
| As1 | −0.24486 (7) | 0.47658 (5) | 0.33857 (3) | 0.00824 (11) |
| As2 | 0.67278 (7) | 0.69498 (5) | 0.01457 (3) | 0.00820 (11) |
| Zn1 | 0.83776 (9) | 0.35654 (6) | 0.10963 (4) | 0.01061 (12) |
| O1 | 0.9575 (5) | 0.3826 (4) | 0.2663 (2) | 0.0117 (6) |
| O2 | 0.4720 (5) | 0.4537 (4) | 0.2972 (3) | 0.0153 (7) |
| O3 | 0.6522 (6) | 0.1665 (4) | 0.1521 (3) | 0.0124 (6) |
| O4 | −0.2204 (6) | 0.3987 (4) | 0.4618 (2) | 0.0132 (6) |
| O5 | 1.1990 (5) | 0.3270 (4) | 0.0989 (2) | 0.0119 (6) |
| O6 | 0.8294 (5) | 0.5986 (4) | 0.1072 (2) | 0.0128 (6) |
| O7 | 0.6245 (5) | 0.3445 (4) | −0.0251 (2) | 0.0112 (6) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Sr1 | 0.00753 (19) | 0.0120 (2) | 0.0140 (2) | −0.00041 (14) | −0.00140 (15) | 0.00130 (15) |
| As1 | 0.00647 (19) | 0.0078 (2) | 0.0104 (2) | 0.00031 (14) | −0.00097 (15) | −0.00028 (15) |
| As2 | 0.0062 (2) | 0.0096 (2) | 0.0088 (2) | 0.00015 (14) | −0.00062 (15) | −0.00011 (15) |
| Zn1 | 0.0082 (2) | 0.0101 (2) | 0.0134 (3) | −0.00048 (18) | −0.00143 (18) | 0.00016 (19) |
| O1 | 0.0082 (14) | 0.0150 (15) | 0.0118 (15) | 0.0032 (11) | 0.0010 (12) | −0.0016 (12) |
| O2 | 0.0066 (14) | 0.0137 (16) | 0.0253 (19) | −0.0001 (11) | −0.0055 (13) | −0.0007 (13) |
| O3 | 0.0118 (15) | 0.0063 (14) | 0.0189 (16) | 0.0007 (11) | 0.0004 (12) | 0.0015 (12) |
| O4 | 0.0183 (15) | 0.0094 (15) | 0.0118 (15) | 0.0033 (12) | −0.0005 (12) | 0.0006 (12) |
| O5 | 0.0077 (14) | 0.0174 (16) | 0.0106 (15) | 0.0000 (11) | 0.0002 (11) | −0.0002 (12) |
| O6 | 0.0117 (15) | 0.0104 (15) | 0.0161 (16) | 0.0004 (11) | −0.0053 (12) | 0.0015 (12) |
| O7 | 0.0044 (13) | 0.0157 (16) | 0.0136 (15) | −0.0011 (11) | −0.0001 (11) | 0.0015 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Sr1—O2 | 2.525 (3) | Zn1—O3 | 1.973 (3) |
| Sr1—O1$^{\rm i}$ | 2.557 (3) | Zn1—O5 | 2.013 (3) |
| Sr1—O2$^{\rm ii}$ | 2.576 (3) | Zn1—O6 | 2.023 (3) |
| Sr1—O6$^{\rm iii}$ | 2.602 (3) | Zn1—O7 | 2.106 (3) |
| Sr1—O3$^{\rm ii}$ | 2.640 (3) | Zn1—O1 | 2.157 (3) |
| Sr1—O7$^{\rm iv}$ | 2.714 (3) | Zn1—Sr1$^{\rm vii}$ | 3.6059 (9) |
| Sr1—O5$^{\rm i}$ | 2.765 (3) | Zn1—Sr1$^{\rm viii}$ | 3.6762 (11) |
| Sr1—O1$^{\rm iii}$ | 2.851 (3) | O1—As1$^{\rm vii}$ | 1.671 (3) |
| Sr1—O5$^{\rm iii}$ | 3.268 (3) | O1—Sr1$^{\rm viii}$ | 2.557 (3) |
| Sr1—As1 | 3.3913 (9) | O1—Sr1$^{\rm vii}$ | 2.851 (3) |

| | | | |
|---|---|---|---|
| Sr1—Zn1$^{iii}$ | 3.6059 (9) | O2—As1$^{vii}$ | 1.654 (3) |
| Sr1—Zn1$^{i}$ | 3.6762 (11) | O2—Sr1$^{ix}$ | 2.576 (3) |
| As1—O2$^{iii}$ | 1.654 (3) | O3—As1$^{ix}$ | 1.670 (3) |
| As1—O3$^{ii}$ | 1.670 (3) | O3—Sr1$^{ix}$ | 2.640 (3) |
| As1—O1$^{iii}$ | 1.671 (3) | O4—As2$^{ix}$ | 1.749 (3) |
| As1—O4 | 1.744 (3) | O5—As2$^{vi}$ | 1.669 (3) |
| As1—Sr1$^{v}$ | 3.6869 (8) | O5—Sr1$^{viii}$ | 2.765 (3) |
| As1—Sr1$^{iii}$ | 3.7374 (10) | O5—Sr1$^{vii}$ | 3.268 (3) |
| As2—O5$^{vi}$ | 1.669 (3) | O6—Sr1$^{vii}$ | 2.602 (3) |
| As2—O7$^{iv}$ | 1.679 (3) | O7—As2$^{iv}$ | 1.679 (3) |
| As2—O6 | 1.682 (3) | O7—Sr1$^{iv}$ | 2.714 (3) |
| As2—O4$^{ii}$ | 1.749 (3) | | |

| | | | |
|---|---|---|---|
| O2—Sr1—O1$^{i}$ | 93.44 (10) | O2$^{iii}$—As1—Sr1 | 127.11 (12) |
| O2—Sr1—O2$^{ii}$ | 155.50 (7) | O3$^{ii}$—As1—Sr1 | 49.74 (11) |
| O1$^{i}$—Sr1—O2$^{ii}$ | 69.30 (10) | O1$^{iii}$—As1—Sr1 | 57.05 (11) |
| O2—Sr1—O6$^{iii}$ | 120.91 (10) | O4—As1—Sr1 | 124.17 (11) |
| O1$^{i}$—Sr1—O6$^{iii}$ | 140.59 (10) | O2$^{iii}$—As1—Sr1$^{v}$ | 37.37 (11) |
| O2$^{ii}$—Sr1—O6$^{iii}$ | 81.88 (10) | O3$^{ii}$—As1—Sr1$^{v}$ | 152.14 (11) |
| O2—Sr1—O3$^{ii}$ | 99.39 (10) | O1$^{iii}$—As1—Sr1$^{v}$ | 91.54 (11) |
| O1$^{i}$—Sr1—O3$^{ii}$ | 120.53 (10) | O4—As1—Sr1$^{v}$ | 88.37 (11) |
| O2$^{ii}$—Sr1—O3$^{ii}$ | 76.47 (10) | Sr1—As1—Sr1$^{v}$ | 138.830 (16) |
| O6$^{iii}$—Sr1—O3$^{ii}$ | 75.40 (10) | O2$^{iii}$—As1—Sr1$^{iii}$ | 33.36 (11) |
| O2—Sr1—O7$^{iv}$ | 98.52 (11) | O3$^{ii}$—As1—Sr1$^{iii}$ | 82.08 (11) |
| O1$^{i}$—Sr1—O7$^{iv}$ | 81.41 (10) | O1$^{iii}$—As1—Sr1$^{iii}$ | 120.33 (11) |
| O2$^{ii}$—Sr1—O7$^{iv}$ | 95.96 (10) | O4—As1—Sr1$^{iii}$ | 126.83 (11) |
| O6$^{iii}$—Sr1—O7$^{iv}$ | 75.32 (9) | Sr1—As1—Sr1$^{iii}$ | 101.16 (2) |
| O3$^{ii}$—Sr1—O7$^{iv}$ | 150.51 (10) | Sr1$^{v}$—As1—Sr1$^{iii}$ | 70.374 (18) |
| O2—Sr1—O5$^{i}$ | 83.80 (10) | O5$^{vi}$—As2—O7$^{iv}$ | 118.74 (15) |
| O1$^{i}$—Sr1—O5$^{i}$ | 59.01 (10) | O5$^{vi}$—As2—O6 | 111.75 (16) |
| O2$^{ii}$—Sr1—O5$^{i}$ | 72.49 (10) | O7$^{iv}$—As2—O6 | 109.62 (15) |
| O6$^{iii}$—Sr1—O5$^{i}$ | 136.65 (10) | O5$^{vi}$—As2—O4$^{ii}$ | 101.56 (15) |
| O3$^{ii}$—Sr1—O5$^{i}$ | 65.08 (9) | O7$^{iv}$—As2—O4$^{ii}$ | 108.69 (15) |
| O7$^{iv}$—Sr1—O5$^{i}$ | 140.40 (9) | O6—As2—O4$^{ii}$ | 105.33 (15) |
| O2—Sr1—O1$^{iii}$ | 65.43 (9) | O5$^{vi}$—As2—Sr1 | 159.71 (11) |
| O1$^{i}$—Sr1—O1$^{iii}$ | 156.84 (6) | O7$^{iv}$—As2—Sr1 | 41.43 (11) |
| O2$^{ii}$—Sr1—O1$^{iii}$ | 127.02 (9) | O6—As2—Sr1 | 78.79 (11) |
| O6$^{iii}$—Sr1—O1$^{iii}$ | 62.52 (9) | O4$^{ii}$—As2—Sr1 | 91.67 (11) |
| O3$^{ii}$—Sr1—O1$^{iii}$ | 58.16 (9) | O3—Zn1—O5 | 116.04 (13) |
| O7$^{iv}$—Sr1—O1$^{iii}$ | 109.88 (9) | O3—Zn1—O6 | 142.82 (13) |
| O5$^{i}$—Sr1—O1$^{iii}$ | 106.95 (9) | O5—Zn1—O6 | 98.26 (13) |
| O2—Sr1—O5$^{iii}$ | 64.66 (10) | O3—Zn1—O7 | 85.04 (13) |
| O1$^{i}$—Sr1—O5$^{iii}$ | 130.69 (9) | O5—Zn1—O7 | 118.29 (12) |
| O2$^{ii}$—Sr1—O5$^{iii}$ | 139.81 (9) | O6—Zn1—O7 | 91.26 (12) |
| O6$^{iii}$—Sr1—O5$^{iii}$ | 61.41 (9) | O3—Zn1—O1 | 87.94 (13) |
| O3$^{ii}$—Sr1—O5$^{iii}$ | 106.87 (9) | O5—Zn1—O1 | 78.02 (12) |
| O7$^{iv}$—Sr1—O5$^{iii}$ | 60.98 (9) | O6—Zn1—O1 | 85.46 (12) |
| O5$^{i}$—Sr1—O5$^{iii}$ | 146.28 (9) | O7—Zn1—O1 | 163.69 (12) |

| | |
|---|---|
| O1$^{iii}$—Sr1—O5$^{iii}$ | 50.28 (8) |
| O2—Sr1—As1 | 83.76 (7) |
| O1$^{i}$—Sr1—As1 | 146.09 (7) |
| O2$^{ii}$—Sr1—As1 | 100.76 (7) |
| O6$^{iii}$—Sr1—As1 | 63.68 (7) |
| O3$^{ii}$—Sr1—As1 | 28.87 (7) |
| O7$^{iv}$—Sr1—As1 | 132.48 (7) |
| O5$^{i}$—Sr1—As1 | 87.12 (7) |
| O1$^{iii}$—Sr1—As1 | 29.47 (6) |
| O5$^{iii}$—Sr1—As1 | 78.27 (6) |
| O2—Sr1—Zn1$^{iii}$ | 87.59 (8) |
| O1$^{i}$—Sr1—Zn1$^{iii}$ | 159.49 (7) |
| O2$^{ii}$—Sr1—Zn1$^{iii}$ | 114.76 (7) |
| O6$^{iii}$—Sr1—Zn1$^{iii}$ | 33.32 (7) |
| O3$^{ii}$—Sr1—Zn1$^{iii}$ | 79.36 (7) |
| O7$^{iv}$—Sr1—Zn1$^{iii}$ | 78.19 (7) |
| O5$^{i}$—Sr1—Zn1$^{iii}$ | 141.29 (7) |
| O1$^{iii}$—Sr1—Zn1$^{iii}$ | 36.73 (6) |
| O5$^{iii}$—Sr1—Zn1$^{iii}$ | 33.60 (5) |
| As1—Sr1—Zn1$^{iii}$ | 54.392 (17) |
| O2—Sr1—Zn1$^{i}$ | 71.08 (8) |
| O1$^{i}$—Sr1—Zn1$^{i}$ | 34.99 (7) |
| O2$^{ii}$—Sr1—Zn1$^{i}$ | 85.35 (7) |
| O6$^{iii}$—Sr1—Zn1$^{i}$ | 166.41 (7) |
| O3$^{ii}$—Sr1—Zn1$^{i}$ | 97.12 (7) |
| O7$^{iv}$—Sr1—Zn1$^{i}$ | 110.80 (7) |
| O5$^{i}$—Sr1—Zn1$^{i}$ | 32.70 (6) |
| O1$^{iii}$—Sr1—Zn1$^{i}$ | 123.39 (6) |
| O5$^{iii}$—Sr1—Zn1$^{i}$ | 132.15 (5) |
| As1—Sr1—Zn1$^{i}$ | 114.63 (2) |
| Zn1$^{iii}$—Sr1—Zn1$^{i}$ | 157.632 (18) |
| O2$^{iii}$—As1—O3$^{ii}$ | 114.79 (16) |
| O2$^{iii}$—As1—O1$^{iii}$ | 113.26 (16) |
| O3$^{ii}$—As1—O1$^{iii}$ | 106.36 (16) |
| O2$^{iii}$—As1—O4 | 108.51 (17) |
| O3$^{ii}$—As1—O4 | 105.51 (16) |
| O1$^{iii}$—As1—O4 | 107.95 (15) |
| O3—Zn1—Sr1$^{vii}$ | 140.05 (10) |
| O5—Zn1—Sr1$^{vii}$ | 63.96 (9) |
| O6—Zn1—Sr1$^{vii}$ | 44.96 (8) |
| O7—Zn1—Sr1$^{vii}$ | 132.18 (9) |
| O1—Zn1—Sr1$^{vii}$ | 52.23 (9) |
| O3—Zn1—Sr1$^{viii}$ | 80.60 (9) |
| O5—Zn1—Sr1$^{viii}$ | 47.89 (9) |
| O6—Zn1—Sr1$^{viii}$ | 116.59 (9) |
| O7—Zn1—Sr1$^{viii}$ | 148.87 (9) |
| O1—Zn1—Sr1$^{viii}$ | 42.84 (8) |
| Sr1$^{vii}$—Zn1—Sr1$^{viii}$ | 71.96 (2) |
| As1$^{vii}$—O1—Zn1 | 113.01 (15) |
| As1$^{vii}$—O1—Sr1$^{viii}$ | 140.09 (17) |
| Zn1—O1—Sr1$^{viii}$ | 102.17 (12) |
| As1$^{vii}$—O1—Sr1$^{vii}$ | 93.48 (13) |
| Zn1—O1—Sr1$^{vii}$ | 91.04 (11) |
| Sr1$^{viii}$—O1—Sr1$^{vii}$ | 104.45 (10) |
| As1$^{vii}$—O2—Sr1 | 125.53 (17) |
| As1$^{vii}$—O2—Sr1$^{ix}$ | 119.69 (16) |
| Sr1—O2—Sr1$^{ix}$ | 114.01 (11) |
| As1$^{ix}$—O3—Zn1 | 128.72 (18) |
| As1$^{ix}$—O3—Sr1$^{ix}$ | 101.39 (14) |
| Zn1—O3—Sr1$^{ix}$ | 124.90 (14) |
| As1—O4—As2$^{ix}$ | 122.39 (18) |
| As2$^{vi}$—O5—Zn1 | 120.70 (17) |
| As2$^{vi}$—O5—Sr1$^{viii}$ | 130.19 (16) |
| Zn1—O5—Sr1$^{viii}$ | 99.40 (12) |
| As2$^{vi}$—O5—Sr1$^{vii}$ | 121.35 (15) |
| Zn1—O5—Sr1$^{vii}$ | 82.44 (10) |
| Sr1$^{viii}$—O5—Sr1$^{vii}$ | 89.94 (9) |
| As2—O6—Zn1 | 120.07 (17) |
| As2—O6—Sr1$^{vii}$ | 133.84 (17) |
| Zn1—O6—Sr1$^{vii}$ | 101.73 (12) |
| As2$^{iv}$—O7—Zn1 | 118.14 (17) |
| As2$^{iv}$—O7—Sr1$^{iv}$ | 114.40 (15) |
| Zn1—O7—Sr1$^{iv}$ | 126.37 (12) |

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

## (BaCuAs2O7) Barium copper diarsenic heptaoxide

*Crystal data*

| | |
|---|---|
| $BaCuAs_2O_7$ | $\beta = 91.12 (3)°$ |
| $M_r = 462.72$ | $V = 634.9 (2)$ Å$^3$ |
| Monoclinic, $P2_1/n$ | $Z = 4$ |
| $a = 5.7343 (11)$ Å | $F(000) = 828$ |
| $b = 8.4722 (17)$ Å | $D_x = 4.841$ Mg m$^{-3}$ |
| $c = 13.071 (3)$ Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |

$\mu$ = 19.84 mm$^{-1}$
$T$ = 298 K

Prismatic, blue-green
0.06 × 0.03 × 0.02 mm

*Data collection*

Nonius KappaCCD
diffractometer
Radiation source: fine-focus sealed X-ray tube
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan
(Otwinowski & Minor, 1997)
$T_{\min}$ = 0.807, $T_{\max}$ = 1.000
4991 measured reflections

1298 independent reflections
1232 reflections with $I > 2\sigma(I)$
$R_{\text{int}}$ = 0.025
$\theta_{\max}$ = 26.4°, $\theta_{\min}$ = 2.9°
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.059
$S$ = 1.20
1297 reflections
101 parameters
0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 6.356P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 2.28 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.72 e Å$^{-3}$
Extinction correction: *SHELXL*,
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0029 (2)

*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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{\text{iso}}$*/$U_{\text{eq}}$ |
|---|---|---|---|---|
| Ba1 | 0.21641 (6) | 0.65177 (4) | 0.21373 (3) | 0.01078 (13) |
| As1 | −0.25303 (10) | 0.46629 (7) | 0.34475 (4) | 0.00811 (16) |
| As2 | 0.67164 (10) | 0.68332 (7) | 0.00787 (4) | 0.00849 (16) |
| Cu1 | 0.78989 (13) | 0.35893 (8) | 0.11961 (6) | 0.01007 (18) |
| O1 | 0.9278 (7) | 0.3766 (5) | 0.2630 (3) | 0.0115 (8) |
| O2 | 0.4698 (7) | 0.4399 (5) | 0.3119 (4) | 0.0170 (9) |
| O3 | 0.6632 (8) | 0.1528 (5) | 0.1488 (3) | 0.0138 (9) |
| O4 | −0.2048 (8) | 0.3849 (5) | 0.4659 (3) | 0.0126 (9) |
| O5 | 1.2020 (8) | 0.3402 (5) | 0.1034 (3) | 0.0142 (9) |
| O6 | 0.8041 (7) | 0.5920 (5) | 0.1077 (3) | 0.0135 (9) |
| O7 | 0.6194 (7) | 0.3516 (5) | −0.0132 (3) | 0.0124 (9) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ba1 | 0.0117 (2) | 0.00914 (19) | 0.0115 (2) | −0.00027 (13) | −0.00038 (13) | 0.00043 (13) |
| As1 | 0.0103 (3) | 0.0060 (3) | 0.0079 (3) | 0.0003 (2) | −0.0006 (2) | −0.0002 (2) |
| As2 | 0.0104 (3) | 0.0082 (3) | 0.0069 (3) | −0.0001 (2) | 0.0000 (2) | 0.0000 (2) |
| Cu1 | 0.0144 (4) | 0.0067 (4) | 0.0090 (4) | −0.0007 (3) | −0.0022 (3) | 0.0006 (3) |
| O1 | 0.012 (2) | 0.011 (2) | 0.011 (2) | 0.0012 (15) | 0.0017 (16) | −0.0003 (16) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 0.010 (2) | 0.016 (2) | 0.024 (2) | 0.0012 (17) | −0.0035 (18) | 0.0004 (19) |
| O3 | 0.019 (2) | 0.007 (2) | 0.016 (2) | 0.0013 (17) | 0.0022 (18) | 0.0016 (17) |
| O4 | 0.022 (2) | 0.0067 (19) | 0.009 (2) | 0.0017 (17) | −0.0015 (17) | 0.0017 (16) |
| O5 | 0.016 (2) | 0.014 (2) | 0.013 (2) | 0.0026 (17) | 0.0058 (17) | 0.0006 (17) |
| O6 | 0.016 (2) | 0.009 (2) | 0.015 (2) | −0.0005 (16) | −0.0050 (17) | −0.0001 (17) |
| O7 | 0.010 (2) | 0.015 (2) | 0.012 (2) | −0.0029 (16) | −0.0003 (17) | 0.0005 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ba1—O2 | 2.628 (4) | Cu1—O3 | 1.932 (4) |
| Ba1—O2$^{i}$ | 2.683 (5) | Cu1—O7 | 1.976 (4) |
| Ba1—O6$^{ii}$ | 2.764 (4) | Cu1—O6 | 1.983 (4) |
| Ba1—O7$^{iii}$ | 2.803 (4) | Cu1—O1 | 2.025 (4) |
| Ba1—O1$^{iv}$ | 2.803 (4) | Cu1—O5 | 2.382 (4) |
| Ba1—O3$^{i}$ | 2.850 (4) | Cu1—Ba1$^{vii}$ | 3.6787 (10) |
| Ba1—O5$^{iv}$ | 2.904 (4) | Cu1—Ba1$^{viii}$ | 3.9494 (12) |
| Ba1—O1$^{ii}$ | 2.938 (4) | O1—As1$^{vii}$ | 1.685 (4) |
| Ba1—O5$^{ii}$ | 3.008 (4) | O1—Ba1$^{viii}$ | 2.803 (4) |
| Ba1—As1 | 3.5818 (10) | O1—Ba1$^{vii}$ | 2.938 (4) |
| Ba1—Cu1$^{ii}$ | 3.6787 (10) | O2—As1$^{vii}$ | 1.654 (4) |
| Ba1—As2 | 3.7950 (13) | O2—Ba1$^{ix}$ | 2.683 (5) |
| As1—O2$^{ii}$ | 1.654 (4) | O3—As1$^{ix}$ | 1.663 (4) |
| As1—O3$^{i}$ | 1.663 (4) | O3—Ba1$^{ix}$ | 2.850 (4) |
| As1—O1$^{ii}$ | 1.685 (4) | O4—As2$^{ix}$ | 1.752 (4) |
| As1—O4 | 1.744 (4) | O5—As2$^{vi}$ | 1.650 (4) |
| As1—Ba1$^{ii}$ | 3.8019 (11) | O5—Ba1$^{viii}$ | 2.904 (4) |
| As1—Ba1$^{v}$ | 3.8295 (9) | O5—Ba1$^{vii}$ | 3.008 (4) |
| As2—O5$^{vi}$ | 1.650 (4) | O6—Ba1$^{vii}$ | 2.764 (4) |
| As2—O6 | 1.685 (4) | O7—As2$^{iii}$ | 1.698 (4) |
| As2—O7$^{iii}$ | 1.698 (4) | O7—Ba1$^{iii}$ | 2.803 (4) |
| As2—O4$^{i}$ | 1.752 (4) | | |
| | | | |
| O2—Ba1—O2$^{i}$ | 153.81 (10) | O2$^{ii}$—As1—Ba1 | 131.49 (17) |
| O2—Ba1—O6$^{ii}$ | 125.38 (13) | O3$^{i}$—As1—Ba1 | 51.16 (15) |
| O2$^{i}$—Ba1—O6$^{ii}$ | 76.68 (13) | O1$^{ii}$—As1—Ba1 | 54.33 (15) |
| O2—Ba1—O7$^{iii}$ | 104.89 (14) | O4—As1—Ba1 | 120.01 (15) |
| O2$^{i}$—Ba1—O7$^{iii}$ | 91.88 (14) | O2$^{ii}$—As1—Ba1$^{ii}$ | 35.13 (16) |
| O6$^{ii}$—Ba1—O7$^{iii}$ | 80.15 (13) | O3$^{i}$—As1—Ba1$^{ii}$ | 82.79 (16) |
| O2—Ba1—O1$^{iv}$ | 90.97 (13) | O1$^{ii}$—As1—Ba1$^{ii}$ | 113.44 (15) |
| O2$^{i}$—Ba1—O1$^{iv}$ | 71.47 (13) | O4—As1—Ba1$^{ii}$ | 133.13 (14) |
| O6$^{ii}$—Ba1—O1$^{iv}$ | 142.42 (13) | Ba1—As1—Ba1$^{ii}$ | 101.86 (2) |
| O7$^{iii}$—Ba1—O1$^{iv}$ | 81.45 (12) | O2$^{ii}$—As1—Ba1$^{v}$ | 36.33 (16) |
| O2—Ba1—O3$^{i}$ | 96.66 (13) | O3$^{i}$—As1—Ba1$^{v}$ | 152.13 (16) |
| O2$^{i}$—Ba1—O3$^{i}$ | 76.64 (13) | O1$^{ii}$—As1—Ba1$^{v}$ | 89.59 (15) |
| O6$^{ii}$—Ba1—O3$^{i}$ | 70.14 (13) | O4—As1—Ba1$^{v}$ | 90.19 (15) |
| O7$^{iii}$—Ba1—O3$^{i}$ | 149.83 (13) | Ba1—As1—Ba1$^{v}$ | 137.295 (19) |
| O1$^{iv}$—Ba1—O3$^{i}$ | 119.53 (12) | Ba1$^{ii}$—As1—Ba1$^{v}$ | 69.617 (19) |
| O2—Ba1—O5$^{iv}$ | 83.98 (14) | O5$^{vi}$—As2—O6 | 115.4 (2) |

| | | | |
|---|---|---|---|
| O2$^{i}$—Ba1—O5$^{iv}$ | 70.11 (13) | O5$^{vi}$—As2—O7$^{iii}$ | 117.7 (2) |
| O6$^{ii}$—Ba1—O5$^{iv}$ | 129.47 (13) | O6—As2—O7$^{iii}$ | 108.5 (2) |
| O7$^{iii}$—Ba1—O5$^{iv}$ | 136.35 (12) | O5$^{vi}$—As2—O4$^{i}$ | 104.0 (2) |
| O1$^{iv}$—Ba1—O5$^{iv}$ | 55.40 (12) | O6—As2—O4$^{i}$ | 104.5 (2) |
| O3$^{i}$—Ba1—O5$^{iv}$ | 65.93 (12) | O7$^{iii}$—As2—O4$^{i}$ | 105.4 (2) |
| O2—Ba1—O1$^{ii}$ | 70.08 (13) | O5$^{vi}$—As2—Ba1 | 159.52 (16) |
| O2$^{i}$—Ba1—O1$^{ii}$ | 121.67 (12) | O6—As2—Ba1 | 74.00 (15) |
| O6$^{ii}$—Ba1—O1$^{ii}$ | 58.97 (12) | O7$^{iii}$—As2—Ba1 | 42.97 (15) |
| O7$^{iii}$—Ba1—O1$^{ii}$ | 113.44 (12) | O4$^{i}$—As2—Ba1 | 90.18 (14) |
| O1$^{iv}$—Ba1—O1$^{ii}$ | 158.02 (6) | O3—Cu1—O7 | 87.90 (19) |
| O3$^{i}$—Ba1—O1$^{ii}$ | 54.80 (12) | O3—Cu1—O6 | 158.73 (19) |
| O5$^{iv}$—Ba1—O1$^{ii}$ | 109.76 (12) | O7—Cu1—O6 | 89.01 (18) |
| O2—Ba1—O5$^{ii}$ | 69.15 (13) | O3—Cu1—O1 | 91.48 (18) |
| O2$^{i}$—Ba1—O5$^{ii}$ | 137.03 (13) | O7—Cu1—O1 | 172.97 (17) |
| O6$^{ii}$—Ba1—O5$^{ii}$ | 65.41 (12) | O6—Cu1—O1 | 89.03 (18) |
| O7$^{iii}$—Ba1—O5$^{ii}$ | 63.22 (12) | O3—Cu1—O5 | 109.54 (17) |
| O1$^{iv}$—Ba1—O5$^{ii}$ | 131.40 (12) | O7—Cu1—O5 | 113.23 (17) |
| O3$^{i}$—Ba1—O5$^{ii}$ | 106.90 (12) | O6—Cu1—O5 | 90.99 (17) |
| O5$^{iv}$—Ba1—O5$^{ii}$ | 151.54 (11) | O1—Cu1—O5 | 73.56 (16) |
| O1$^{ii}$—Ba1—O5$^{ii}$ | 53.01 (11) | O3—Cu1—Ba1$^{vii}$ | 142.53 (14) |
| O2—Ba1—As1 | 83.13 (10) | O7—Cu1—Ba1$^{vii}$ | 128.98 (13) |
| O2$^{i}$—Ba1—As1 | 99.08 (10) | O6—Cu1—Ba1$^{vii}$ | 47.66 (12) |
| O6$^{ii}$—Ba1—As1 | 61.04 (9) | O1—Cu1—Ba1$^{vii}$ | 52.83 (12) |
| O7$^{iii}$—Ba1—As1 | 135.40 (9) | O5—Cu1—Ba1$^{vii}$ | 54.59 (11) |
| O1$^{iv}$—Ba1—As1 | 142.98 (9) | O3—Cu1—Ba1$^{viii}$ | 75.98 (14) |
| O3$^{i}$—Ba1—As1 | 27.04 (8) | O7—Cu1—Ba1$^{viii}$ | 143.84 (13) |
| O5$^{iv}$—Ba1—As1 | 87.60 (9) | O6—Cu1—Ba1$^{viii}$ | 117.12 (13) |
| O1$^{ii}$—Ba1—As1 | 27.77 (8) | O1—Cu1—Ba1$^{viii}$ | 42.25 (12) |
| O5$^{ii}$—Ba1—As1 | 80.23 (8) | O5—Cu1—Ba1$^{viii}$ | 46.97 (11) |
| O2—Ba1—Cu1$^{ii}$ | 93.45 (10) | Ba1$^{vii}$—Cu1—Ba1$^{viii}$ | 69.55 (2) |
| O2$^{i}$—Ba1—Cu1$^{ii}$ | 108.16 (9) | As1$^{vii}$—O1—Cu1 | 112.7 (2) |
| O6$^{ii}$—Ba1—Cu1$^{ii}$ | 32.03 (9) | As1$^{vii}$—O1—Ba1$^{viii}$ | 133.9 (2) |
| O7$^{iii}$—Ba1—Cu1$^{ii}$ | 85.05 (9) | Cu1—O1—Ba1$^{viii}$ | 108.69 (17) |
| O1$^{iv}$—Ba1—Cu1$^{ii}$ | 166.46 (9) | As1$^{vii}$—O1—Ba1$^{vii}$ | 97.90 (18) |
| O3$^{i}$—Ba1—Cu1$^{ii}$ | 72.65 (9) | Cu1—O1—Ba1$^{vii}$ | 93.86 (15) |
| O5$^{iv}$—Ba1—Cu1$^{ii}$ | 137.83 (9) | Ba1$^{viii}$—O1—Ba1$^{vii}$ | 98.69 (13) |
| O1$^{ii}$—Ba1—Cu1$^{ii}$ | 33.32 (8) | As1$^{vii}$—O2—Ba1 | 123.6 (2) |
| O5$^{ii}$—Ba1—Cu1$^{ii}$ | 40.19 (8) | As1$^{vii}$—O2—Ba1$^{ix}$ | 122.2 (2) |
| As1—Ba1—Cu1$^{ii}$ | 50.434 (18) | Ba1—O2—Ba1$^{ix}$ | 110.24 (15) |
| O2—Ba1—As2 | 90.73 (10) | As1$^{ix}$—O3—Cu1 | 138.7 (3) |
| O2$^{i}$—Ba1—As2 | 97.19 (10) | As1$^{ix}$—O3—Ba1$^{ix}$ | 101.80 (18) |
| O6$^{ii}$—Ba1—As2 | 104.54 (9) | Cu1—O3—Ba1$^{ix}$ | 114.94 (18) |
| O7$^{iii}$—Ba1—As2 | 24.39 (9) | As1—O4—As2$^{ix}$ | 125.3 (2) |
| O1$^{iv}$—Ba1—As2 | 61.30 (9) | As2$^{vi}$—O5—Cu1 | 122.7 (2) |
| O3$^{i}$—Ba1—As2 | 172.51 (9) | As2$^{vi}$—O5—Ba1$^{viii}$ | 126.4 (2) |
| O5$^{iv}$—Ba1—As2 | 116.28 (8) | Cu1—O5—Ba1$^{viii}$ | 96.18 (14) |
| O1$^{ii}$—Ba1—As2 | 127.56 (8) | As2$^{vi}$—O5—Ba1$^{vii}$ | 121.3 (2) |
| O5$^{ii}$—Ba1—As2 | 74.62 (8) | Cu1—O5—Ba1$^{vii}$ | 85.23 (12) |

| | | | |
|---|---|---|---|
| As1—Ba1—As2 | 154.659 (18) | Ba1$^{viii}$—O5—Ba1$^{vii}$ | 94.90 (13) |
| Cu1$^{ii}$—Ba1—As2 | 105.81 (2) | As2—O6—Cu1 | 120.0 (2) |
| O2$^{ii}$—As1—O3$^{i}$ | 115.9 (2) | As2—O6—Ba1$^{vii}$ | 132.3 (2) |
| O2$^{ii}$—As1—O1$^{ii}$ | 112.0 (2) | Cu1—O6—Ba1$^{vii}$ | 100.32 (17) |
| O3$^{i}$—As1—O1$^{ii}$ | 105.5 (2) | As2$^{iii}$—O7—Cu1 | 116.1 (2) |
| O2$^{ii}$—As1—O4 | 108.5 (2) | As2$^{iii}$—O7—Ba1$^{iii}$ | 112.6 (2) |
| O3$^{i}$—As1—O4 | 106.6 (2) | Cu1—O7—Ba1$^{iii}$ | 130.72 (19) |
| O1$^{ii}$—As1—O4 | 108.0 (2) | | |

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