The crystal structure of $BaH_6As_4O_{14}$ redetermined, revealing the localization of the hydrogen atoms

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The crystal structure of barium hexahydrogen *cyclo*-tetradecaoxidotetra-arsenate(V), was redetermined. In comparison with the previous determination [Blum, Durif & Guitel. (1977). *Acta Cryst.* B**33**, 3222–3224] the positions of the hydrogen atoms were located, and more precise data in terms of bond lengths and angles were obtained. The crystal structure is composed of an eight-coordinate Ba^{2+} cation and a condensed oxoarsenate anion with connectivity $[As^{[4]}(OH)_{1/1}O_{1/1}O_{2/2}As^{[6]}(OH)_{2/1}O_{1/2}]_2^{2-}$. O—H···O hydrogen bonds between isolated anions consolidate the crystal packing.

3D view
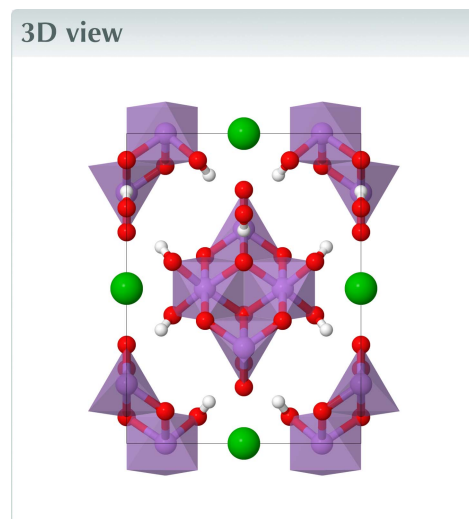
Structure description

During phase-formation studies of hydrous and anhydrous barium arsenates (Weil, 2016), high-quality single crystals of $BaH_6As_4O_{14}$ were grown. The structure of this compound has been determined previously (Blum *et al.*, 1977), however without localization of the hydrogen atoms. In the current study, the positions of the hydrogen atoms were located unambiguously and the structure redetermined, leading to more precise data as can be seen by a comparison of selected bond lengths of the two refinements (Table 1), and to a better understanding of the hydrogen-bonding scheme.

The main building units of the crystal structure of $BaH_6As_4O_{14}$ are one Ba^{2+} cation (site symmetry $2/m$) and a condensed anion $H_6As_4O_{14}^{2-}$ with point group symmetry $2/m$. In the anion, two edge-sharing $[As1O_6]$ octahedra are bridged by two $[As2O_4]$ tetrahedra. The non-bridging O atom ($OE1$) and its three symmetry-related counterparts of the two $[As1O_6]$ octahedra are bonded to hydrogen atoms (H2); one of the two terminal O atoms of the the $[AsO_4]$ tetrahedron ($OE22$) likewise carries a hydrogen atom (H1). The connectivity of the anion can be formulated as $[As^{[4]}(OH)_{1/1}O_{1/1}O_{2/2}As^{[6]}(OH)_{2/1}O_{1/2}]_2^{2-}$. Adjacent anions are linked by an intricate network of strong to medium O—H···O hydrogen bonds (Table 2, Fig. 1) between the outward OH groups and the second

Table 1
Comparison of selected bond lengths (Å) from the current and the previous (Blum *et al.*, 1977) refinement of $BaH_6As_4O_{14}$.

In the previous refinement, a = 8.496 (3), b = 11.249 (8), c = 5.858 (3) Å; T = 298 K; R = 0.051.

	Current refinement	Previous refinement
Ba—OE1	2.7807 (6)	2.800 (3)
Ba—OE21^{iv}	2.9154 (9)	2.935 (3)
Ba—OE22^{vi}	2.9229 (9)	2.948 (4)
As1—OE1	1.7628 (6)	1.767 (3)
As1—OL11	1.8346 (6)	1.839 (3)
As1—OL12	1.8804 (6)	1.887 (3)
As2—OE21	1.6497 (9)	1.656 (5)
As2—OE22^{x}	1.7011 (9)	1.703 (5)
As2—OL12	1.7119 (9)	1.721 (3)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
OE22—H1$\cdots$OL11	0.85 (1)	1.71 (1)	2.5552 (13)	178 (3)
OE1—H2$\cdots$OE21^{i}	0.85 (1)	1.83 (1)	2.6319 (10)	158 (2)

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$.

non-bridging O atom of the [AsO$_4$] tetrahedra (OE21) and the bridging O atoms of the two [AsO$_6$] octahedra (O11). Bond lengths and angles in the anion are consistent with published data as detailed in a review on oxoarsenate anions comprising of tetrahedral and octahedral building units (Schwendtner &
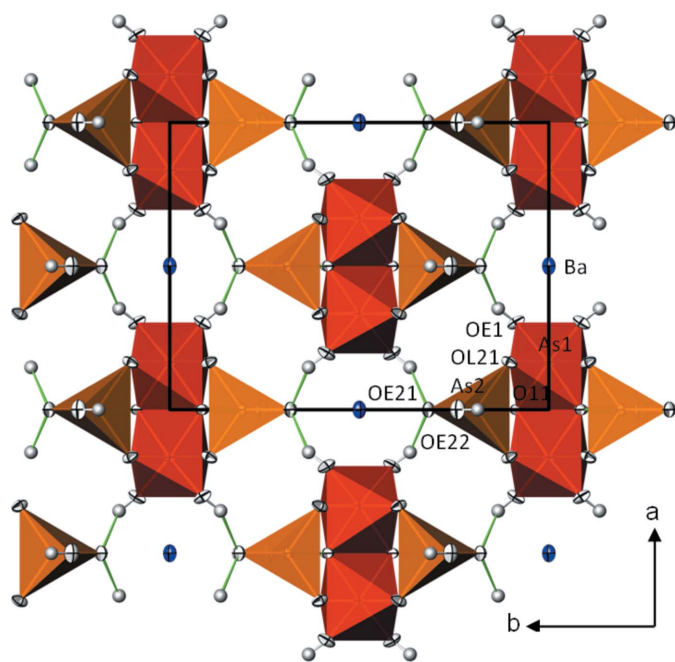
Figure 1
The crystal structure of $BaH_6As_4O_{14}$ in a projection along [00$\bar{1}$]. Displacement ellipsoids are drawn at the 97% probability level. [AsO$_4$] tetrahedra are orange, [AsO$_6$] octahedra are red, and O—H$\cdots$O hydrogen-bonding interactions are shown as green lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	$BaH_6As_4O_{14}$
M_r	667.07
Crystal system, space group	Orthorhombic, *Pman*
Temperature (K)	100
a, b, c (Å)	8.4638 (5), 11.1799 (7), 5.8353 (4)
V (Å^3)	552.16 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	15.57
Crystal size (mm)	0.12 × 0.10 × 0.09
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.551, 0.749
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18011, 2384, 2146
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.995
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.015, 0.032, 1.05
No. of reflections	2384
No. of parameters	60
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.11, −0.98

Coordinates taken from previous refinement. Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXL2017* (Sheldrick, 2015), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

Kolitsch, 2007). The Ba^{2+} cation is situated in the voids of the hydrogen-bonded anionic network and is surrounded by eight O atoms in form of a trigonal prism that is capped on one face by two O atoms.

Synthesis and crystallization

Single crystals of $BaH_6As_4O_{14}$ with a maximal edge-length of 2 mm and a pinacoidal form were grown by refluxing 1.5 g of Ba(OH)$_2\cdot$8H$_2$O in a mixture of 20 ml of glacial acetic acid and 13.5 ml of H$_3$AsO$_4$ (80%$_{wt}$) for three days.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

The same non-standard setting *Pman* of space group number 53 (standard setting *Pmna*) and atom-labelling scheme as given in the original structure study (Blum *et al.*, 1977) were used. The published atomic coordinates were used as starting parameters for refinement. The H atoms bonded to OE1 and OE22 were clearly discernible from difference-Fourier maps. The corresponding hydrogen atoms were refined with a distance restraint d(O—H) = 0.85 (1) Å, and with an independent U_{iso} parameter for each H atom.

References

Blum, D., Durif, A. & Guitel, J. C. (1977). *Acta Cryst.* B**33**, 3222–3224.

Bruker (2014). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dowty, E. (2006). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.

Schwendtner, K. & Kolitsch, U. (2007). *Acta Cryst.* B**63**, 205–215.

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

Weil, M. (2016). *Cryst. Growth Des.* **16**, 908–921.

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

full crystallographic data

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Barium hexahydrogen *cyclo*-tetradecaoxidotetraarsenate(V)

Crystal data

BaH$_6$As$_4$O$_{14}$	$F(000) = 612$
$M_r = 667.07$	$D_x = 4.012$ Mg m^{-3}
Orthorhombic, *Pman*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ab 2	Cell parameters from 8994 reflections
$a = 8.4638$ (5) Å	$\theta = 3.0–45.0°$
$b = 11.1799$ (7) Å	$\mu = 15.57$ mm^{-1}
$c = 5.8353$ (4) Å	$T = 100$ K
$V = 552.16$ (6) Å^3	Fragment, colourless
$Z = 2$	$0.12 \times 0.10 \times 0.09$ mm

Data collection

Bruker APEXII CCD diffractometer	18011 measured reflections
Radiation source: fine-focus sealed tube	2384 independent reflections
Graphite monochromator	2146 reflections with $I > 2\sigma(I)$
ω– and φ–scans	$R_{int} = 0.030$
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)	$\theta_{max} = 45.0°$, $\theta_{min} = 3.0°$
	$h = -16 \rightarrow 15$
	$k = -22 \rightarrow 21$
$T_{min} = 0.551$, $T_{max} = 0.749$	$l = -5 \rightarrow 11$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.015$	$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 0.1747P]$
$wR(F^2) = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2384 reflections	$\Delta\rho_{max} = 1.11$ e Å^{-3}
60 parameters	$\Delta\rho_{min} = -0.98$ e Å^{-3}
2 restraints	Extinction correction: SHELXL2017 (Sheldrick, 2015), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Hydrogen site location: difference Fourier map	Extinction coefficient: 0.0072 (3)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Ba	0.500000	0.000000	0.000000	0.00498 (2)
As1	0.16637 (2)	0.000000	0.500000	0.00269 (2)
As2	0.000000	0.19072 (2)	0.78506 (2)	0.00290 (2)
OL12	0.16513 (7)	0.10385 (6)	0.75348 (10)	0.00498 (9)
OE21	0.000000	0.31803 (8)	0.64215 (16)	0.00545 (13)
OE22	0.000000	0.24048 (8)	0.06056 (16)	0.00613 (13)
OL11	0.000000	0.08529 (8)	0.38202 (15)	0.00430 (12)
OE1	0.30358 (7)	0.08639 (6)	0.34427 (11)	0.00573 (9)
H1	0.000000	0.1876 (17)	0.165 (3)	0.028 (8)*
H2	0.352 (2)	0.1338 (14)	0.434 (3)	0.032 (5)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0.00751 (4)	0.00420 (4)	0.00322 (4)	0.000	0.000	−0.00032 (3)
As1	0.00190 (4)	0.00349 (4)	0.00268 (4)	0.000	0.000	−0.00003 (3)
As2	0.00286 (4)	0.00294 (4)	0.00290 (4)	0.000	0.000	0.00008 (3)
OL12	0.0041 (2)	0.0061 (2)	0.0047 (2)	0.00150 (17)	−0.00042 (15)	−0.00182 (16)
OE21	0.0057 (3)	0.0045 (3)	0.0061 (3)	0.000	0.000	0.0022 (3)
OE22	0.0093 (4)	0.0054 (3)	0.0038 (3)	0.000	0.000	−0.0007 (3)
OL11	0.0028 (3)	0.0051 (3)	0.0050 (3)	0.000	0.000	0.0014 (2)
OE1	0.0046 (2)	0.0072 (2)	0.0054 (2)	−0.00268 (17)	0.00091 (17)	−0.00025 (18)

Geometric parameters (Å, º)

Ba—OE1	2.7807 (6)	As1—OE1	1.7628 (6)
Ba—OE1^i	2.7808 (6)	As1—OL11	1.8346 (6)
Ba—OE1^{ii}	2.7808 (6)	As1—OL11^{ix}	1.8346 (6)
Ba—OE1^{iii}	2.7808 (6)	As1—OL12	1.8804 (6)
Ba—OE21^{iv}	2.9153 (9)	As1—OL12^{viii}	1.8804 (6)
Ba—OE21^v	2.9153 (9)	As2—OE21	1.6497 (9)
Ba—OE22^{vi}	2.9229 (9)	As2—OE22^x	1.7012 (9)
Ba—OE22^{vii}	2.9229 (9)	As2—OL12	1.7119 (6)
Ba—As2^{iv}	3.6782 (2)	As2—OL12^{xi}	1.7119 (6)
Ba—As2^v	3.6782 (2)	OE22—H1	0.8501 (10)
As1—OE1^{viii}	1.7628 (6)	OE1—H2	0.8498 (10)
OE1—Ba—OE1^i	73.43 (3)	OE1^{viii}—As1—OL11	169.69 (3)
OE1—Ba—OE1^{ii}	106.57 (3)	OE1—As1—OL11	91.57 (3)

OE1^i—Ba—OE1^{ii}	180.000 (18)	OE1^{viii}—As1—OL11^{ix}	91.57 (3)
OE1—Ba—OE1^{iii}	180.0	OE1—As1—OL11^{ix}	169.69 (3)
OE1^i—Ba—OE1^{iii}	106.57 (3)	OL11—As1—OL11^{ix}	79.74 (4)
OE1^{ii}—Ba—OE1^{iii}	73.43 (3)	OE1^{viii}—As1—OL12	86.36 (3)
OE1—Ba—OE21^{iv}	105.967 (19)	OE1—As1—OL12	94.06 (3)
OE1^i—Ba—OE21^{iv}	105.967 (19)	OL11—As1—OL12	88.28 (3)
OE1^{ii}—Ba—OE21^{iv}	74.033 (19)	OL11^{ix}—As1—OL12	91.23 (3)
OE1^{iii}—Ba—OE21^{iv}	74.033 (19)	OE1^{viii}—As1—OL12^{viii}	94.06 (3)
OE1—Ba—OE21^v	74.033 (19)	OE1—As1—OL12^{viii}	86.36 (3)
OE1^i—Ba—OE21^v	74.033 (19)	OL11—As1—OL12^{viii}	91.23 (3)
OE1^{ii}—Ba—OE21^v	105.967 (19)	OL11^{ix}—As1—OL12^{viii}	88.28 (3)
OE1^{iii}—Ba—OE21^v	105.967 (19)	OL12—As1—OL12^{viii}	179.36 (4)
OE21^{iv}—Ba—OE21^v	180.00 (3)	OE21—As2—OE22^x	101.28 (5)
OE1—Ba—OE22^{vi}	64.396 (19)	OE21—As2—OL12	115.79 (3)
OE1^i—Ba—OE22^{vi}	64.396 (19)	OE22^x—As2—OL12	106.69 (3)
OE1^{ii}—Ba—OE22^{vi}	115.604 (19)	OE21—As2—OL12^{xi}	115.79 (3)
OE1^{iii}—Ba—OE22^{vi}	115.604 (19)	OE22^x—As2—OL12^{xi}	106.69 (3)
OE21^{iv}—Ba—OE22^{vi}	52.69 (3)	OL12—As2—OL12^{xi}	109.46 (4)
OE21^v—Ba—OE22^{vi}	127.31 (3)	As2—OL12—As1	116.07 (3)
OE1—Ba—OE22^{vii}	115.604 (19)	As2—OE21—Ba^{xii}	103.89 (4)
OE1^i—Ba—OE22^{vii}	115.604 (19)	As2^{xiii}—OE22—Ba^{vi}	102.14 (4)
OE1^{ii}—Ba—OE22^{vii}	64.396 (19)	As2^{xiii}—OE22—H1	116.8 (17)
OE1^{iii}—Ba—OE22^{vii}	64.396 (19)	Ba^{vi}—OE22—H1	141.1 (17)
OE21^{iv}—Ba—OE22^{vii}	127.31 (3)	As1^{ix}—OL11—As1	100.26 (4)
OE21^v—Ba—OE22^{vii}	52.69 (3)	As1—OE1—Ba	125.17 (3)
OE22^{vi}—Ba—OE22^{vii}	180.0	As1—OE1—H2	110.1 (14)
OE1^{viii}—As1—OE1	97.58 (4)	Ba—OE1—H2	111.8 (14)

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

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
OE22—H1⋯OL11	0.85 (1)	1.71 (1)	2.5552 (13)	178 (3)
OE1—H2⋯OE21^{vi}	0.85 (1)	1.83 (1)	2.6319 (10)	158 (2)

Symmetry code: (vi) −x+1/2, −y+1/2, z.