inorganic compounds

RbH$_2$AsO$_4$

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RbH$_2$AsO$_4$, rubidium dihydrogenarsenate (RDA), was synthesized by partial neutralization of an aqueous H$_3$AsO$_4$ solution with aqueous Rb$_2$CO$_3$. Its paraelectric room-temperature phase is composed of virtually regular tetrahedral [AsO$_2$(OH)$_2$]$^-$ anions and Rb$^+$ cations, both located on $\bar{4}$ positions. The [AsO$_2$(OH)$_2$] units are connected *via* O—H⋯O hydrogen bonds into a three-dimensional network, whereby the H atoms are equally disordered between the O atoms. The Rb$^+$ cations are located in channels running along the <100> directions and coordinated by eight O atoms located at the vertices of a snub disphenoid.

Related literature

For isotypic phases, see: Al-Karaghouli *et al.* (1978); Delain (1958); Ferrari *et al.* (1956); Helmholtz & Levine (1942); Novotny & Szekely (1952); West (1930); Tenzer *et al.* (1958). For related phases, see: Stöger *et al.* (2012). For isoformular phases crystallizing in a different structure type, *viz.*LiH$_2$PO$_4$, see: Catti & Ivaldi (1977); Catti & Ferraris (1974); Nelmes & Choudhary (1978); Fanchon *et al.* (1987). For phase transition, see: Fairall & Reese (1974). For physical properties of RDA and isotypic analogs, see: Ichikawa *et al.* (2001); Shen (1984); Negres *et al.* (2005). For crystal growth, see: Rashkovich (1991). For bond-valence analyses, see: Brown & Altermatt (1985). The extinction correction is described by Becker & Coppens (1974).

Experimental

Crystal data

RbH$_2$AsO$_4$	Z = 4
M_r = 226.4	Mo $K\alpha$ radiation
Tetragonal, $I\bar{4}2d$	μ = 18.07 mm^{-1}
a = 7.7865 (9) Å	T = 295 K
c = 7.466 (2) Å	0.50 × 0.29 × 0.27 mm
V = 452.64 (14) Å^3	

Data collection

Bruker Kappa APEXII CCD diffractometer	9202 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)	955 independent reflections
	567 reflections with $I > 3\sigma(I)$
T_{min} = 0.004, T_{max} = 0.009	R_{int} = 0.076

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025	$\Delta\rho_{max}$ = 1.02 e Å^{-3}
$wR(F^2)$ = 0.032	$\Delta\rho_{min}$ = −0.53 e Å^{-3}
S = 1.25	Absolute structure: Flack (1983), 409 Friedel pairs
955 reflections	
20 parameters	Absolute structure parameter: −0.010 (13)
1 restraint	
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

Rb—O	3.0890 (17)	As—O	1.6828 (11)
Rb—O^i	2.9304 (12)		
O—As—O^{ii}	109.80 (5)	O—As—O^{iii}	109.31 (5)

Symmetry codes: (i) $-x + \frac{1}{2}, y, -z + \frac{3}{4}$; (ii) $-x, -y, z$; (iii) $y, -x, -z$.

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT-Plus* (Bruker, 2013); data reduction: *SAINT-Plus*; program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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supporting information

RbH$_2$AsO$_4$

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S1. Comment

During formation studies and subsequent structure analysis of compounds in the system K$_2$O–As$_2$O$_5$–H$_2$O (Stöger *et al.*, 2012), related alkali phosphates and arsenates with formula type MH$_2$XO$_4$ (M = K, Rb, Cs, NH$_4$; X = P, As) came into attention. With the exception of CsH$_2$PO$_4$, dihydrogenphosphates and -arsenates MH$_2$XO$_4$ (M = K, Rb, Cs, NH$_4$; X = P, As) are isotypic at room temperature and said to belong to the KH$_2$PO$_4$ (KDP) family. Members of the KDP family are ferroelectrics with low T_c (Ichikawa *et al.*, 2001) and feature non-linear optical (NLO) properties (Shen, 1984). They have been intensely studied for their physical properties paired with a simple crystal-chemistry. Moreover, they are of technical importance in optical applications due to their favourable transparency, high damage threshold (Negres *et al.*, 2005) and ready access to large single crystals (Rashkovich, 1991). Notably, KDP is used as a standard NLO active compound to evaluate the performance of novel NLO materials.

Structural data was published for all members of the KDP family with the exception of RbH$_2$AsO$_4$ (RDA): KH$_2$PO$_4$ (West, 1930), RbH$_2$PO$_4$ (Al-Karaghouli *et al.*, 1978), (NH$_4$)H$_2$PO$_4$ (Tenzer *et al.*, 1958), KH$_2$AsO$_4$ (Helmholtz & Levine, 1942), CsH$_2$AsO$_4$ (Ferrari *et al.*, 1956) and (NH$_4$)H$_2$AsO$_4$ (Delain, 1958). The germanate SrH$_2$GeO$_4$ (Novotny & Szekely, 1952) crystallizes likewise in the KDP structure type. The dihydrogenphosphates and arsenates with larger or smaller alkali metals crystallize in different structure types: LiH$_2$PO$_4$ (Catti & Ivaldi, 1977), NaH$_2$PO$_4$ (Catti & Ferraris, 1974), CsH$_2$PO$_4$ (Nelmes & Choudhary, 1978) and LiH$_2$AsO$_4$ (Fanchon *et al.*, 1987).

At room temperature RDA, like all members of the KDP family, exists in the tetragonal paraelectric phase. Below T_c = 110 K it transforms into the orthogonal ferroelectric phase (Fairall & Reese, 1974). The room temperature phase of RDA crystallizes in $I\bar{4}2d$ symmetry. The crystal structure is made up of one [AsO$_2$(OH$_2$)]$^-$ anion and one Rb$^+$ cation, both located on $\bar{4}$ positions. The [AsO$_2$(OH$_2$)] tetrahedra are virtually regular (As—O bond lengths 1.6828 (11) Å; O—As—O angles 109.80 (5)° and 109.31 (5)°). They are connected *via* hydrogen bonding in the <100> directions, forming a three dimensional network (Figs. 1 and 2). Thus, every O atom is either donor or acceptor of an O—H···O hydrogen bond, whereby the proton is equally disordered between both oxygen atoms.

The total bond valence sum (BVS) of the unique O atom calculated using $\Sigma\exp((r_0-r)/b)$ and the parameters of Brown and Altermatt (1985) for Rb^I—O (r_0=2.263 Å, b=0.37) and As^V—O (r_0=1.767 Å, b=0.37) is 1.527 (4) valence units (v.u.). This value is in good agreement with the observed disorder, as it lies halfway between the ideal values of O^{2-} and O$^-$ (2 and 1 v.u., respectively).

The Rb$^+$ cation is located in channels running along the <100> directions (Fig. 1). It is coordinated by eight O atoms located at the vertices of a snub disphenoid (Fig. 3). The total BVS of Rb$^+$ calculates as 1.0878 (15) v.u. using the parameters above, which is in excellent agreement with the expected value (1 v.u.). More remote O atoms are located at 4.3005 (12) Å from the Rb$^+$ ion and can therefore not be considered part of the coordination sphere (contribution of 0.004 v.u.).

S2. Experimental

Rb_2CO_3 and H_3AsO_4 were obtained commercially and used without purification. 1 g 80% *aq*. H_3AsO_4 was dissolved in 10 ml water and titrated against *aq*. Rb_2CO_3 using one drop of methyl red in EtOH as indicator. The water was evaporated and the residue recrystallized from a small amount of water and washed with acetone to obtain large single crystals of RbH_2AsO_4.

S3. Refinement

An initial model was generated by using the published coordinates of the non-H atoms of the isotypic room temperature phase of RbH_2PO_4 (Al-Karaghouli *et al.*, 1978).

The structure was refined against *F* values using the Jana2006 software package (Petříček *et al.*, 2006). The disordered H atom was located in a difference Fourier map and was refined with an occupancy of 0.5. The O—H distance was restrained to 0.850 (1) Å. All non-H atoms were refined with anisotropic displacement parameters.
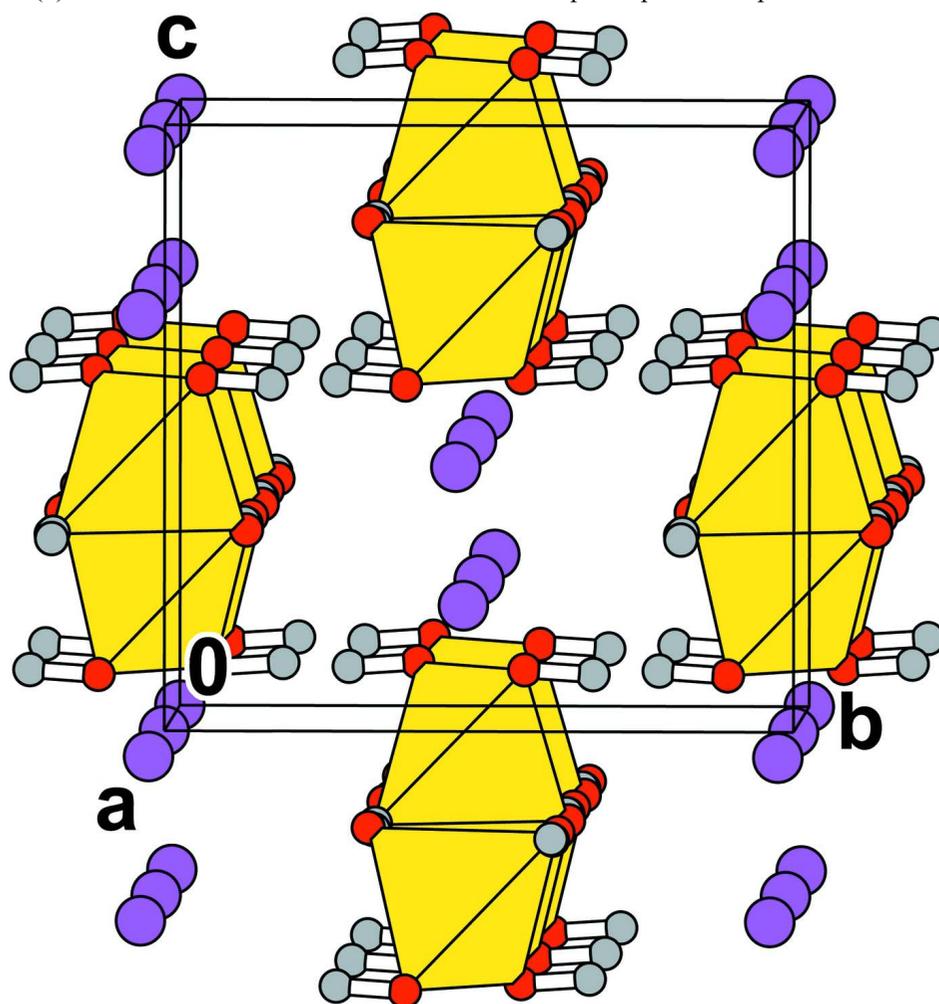

Figure 1

The crystal structure of the paraelectric room temperature phase of RDA viewed approximately down [100]. [AsO₄] tetrahedra are drawn in yellow; Rb, O and H atoms are represented by purple, red and white spheres of arbitrary radii.
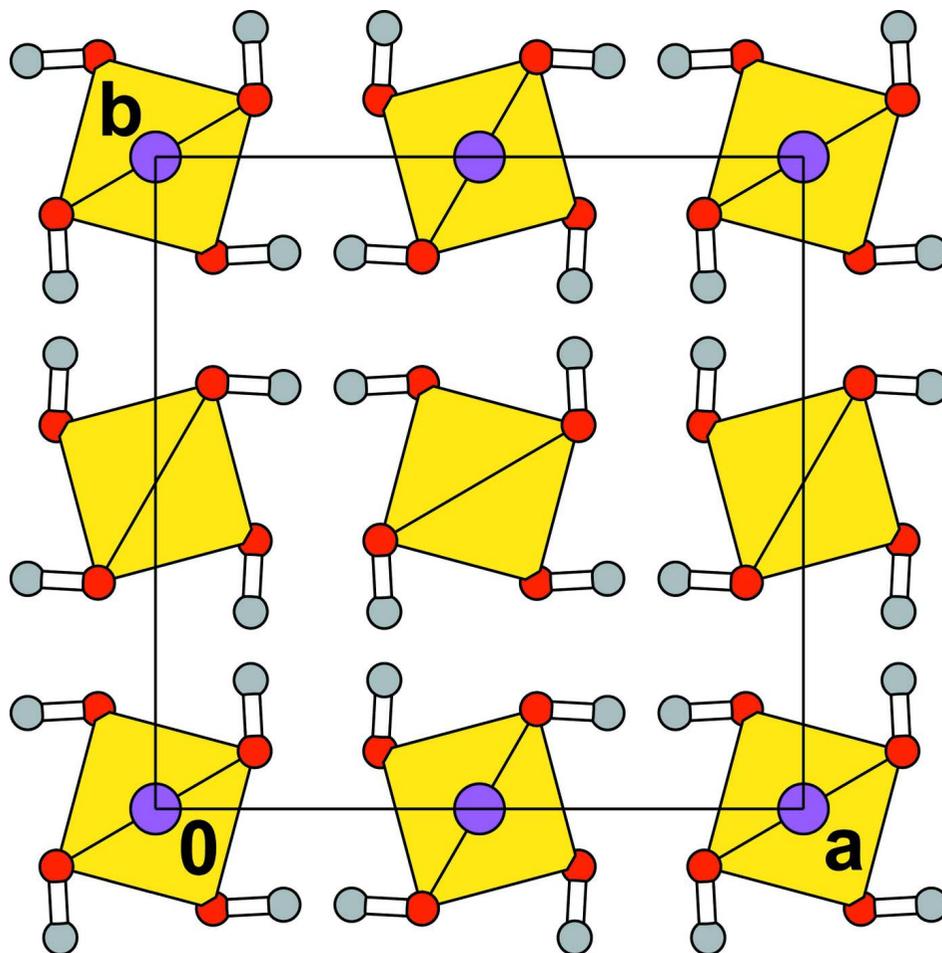
Figure 2

Crystal structure of the paraelectric room temperature phase of RDA viewed down the tetragonal axis [001]. Atom colour codes as in Fig. 1.
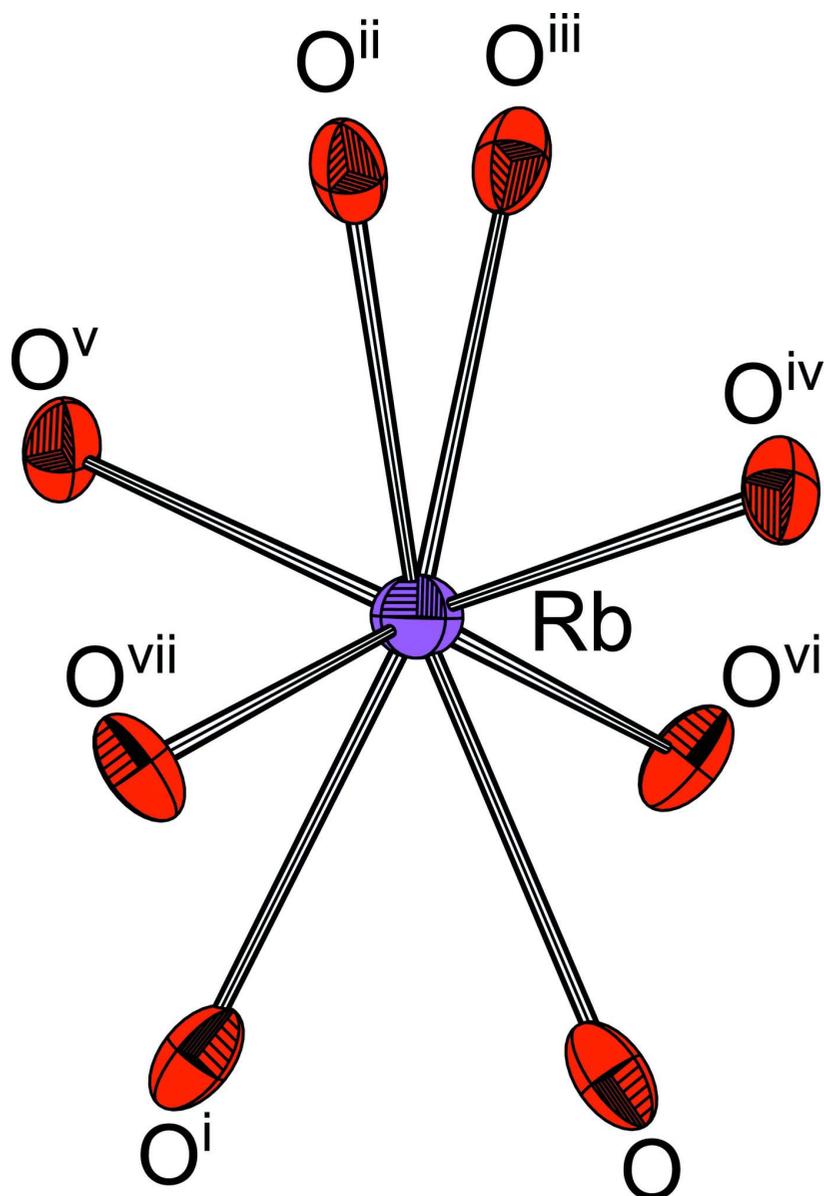
Figure 3

Coordination polyhedron of Rb in the paraelectric room temperature phase of RDA. Rb and O are represented by purple and red ellipsoids drawn at 75% probability level. Symmetry codes: (i) -*x*, -*y*, *z*; (ii) *y*, -*x*, -*z* + 1; (iii) -*y*, *x*, -*z* + 1; (iv) -*x* + 1/2, *y*, -*z* + 3/4; (v) *x* - 1/2, -*y*, -*z* + 3/4; (vi) -*y*, -*x* + 1/2, *z* + 1/4; (vii) *y*, *x* - 1/2, *z* + 1/4

Rubidium dihydrogenarsenate

Crystal data

RbH_2AsO_4	$Z = 4$
$M_r = 226.4$	$F(000) = 416$
Tetragonal, $I\bar{4}2d$	$D_x = 3.321$ Mg m^{-3}
Hall symbol: I -4 2bw	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.7865$ (9) Å	Cell parameters from 2250 reflections
$c = 7.466$ (2) Å	$\theta = 3.7$–44.1°
$V = 452.64$ (14) Å^3	$\mu = 18.07$ mm^{-1}

$T = 295$ K

Block, clear colourless

$0.50 \times 0.29 \times 0.27$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	9202 measured reflections
Radiation source: X-ray tube	955 independent reflections
Graphite monochromator	567 reflections with $I > 3\sigma(I)$
ω and φ scans	$R_{int} = 0.076$
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)	$\theta_{max} = 45.3°$, $\theta_{min} = 3.8°$
	$h = -15 \rightarrow 15$
	$k = -15 \rightarrow 14$
$T_{min} = 0.004$, $T_{max} = 0.009$	$l = -14 \rightarrow 14$

Refinement

Refinement on F	All H-atom parameters refined
Least-squares matrix: full	Weighting scheme based on measured s.u.'s $w =$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$1/(\sigma^2(F) + 0.0001F^2)$
$wR(F^2) = 0.032$	$(\Delta/\sigma)_{max} = 0.021$
$S = 1.25$	$\Delta\rho_{max} = 1.02$ e Å⁻³
955 reflections	$\Delta\rho_{min} = -0.53$ e Å⁻³
20 parameters	Extinction correction: B-C type 1 Gaussian
1 restraint	isotropic (Becker & Coppens, 1974)
0 constraints	Extinction coefficient: 4440 (110)
Primary atom site location: isomorphous structure methods	Absolute structure: Flack (1983), 409 Friedel pairs
Hydrogen site location: difference Fourier map	Absolute structure parameter: −0.010 (13)

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

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Rb	0	0	0.5	0.01896 (5)	
As	0	0	0	0.01382 (5)	
O	0.15295 (14)	0.08872 (11)	0.12961 (14)	0.0203 (2)	
H	0.147 (6)	0.1975 (7)	0.122 (10)	0.048 (12)*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb	0.02023 (8)	0.02023 (8)	0.01640 (11)	0	0	0
As	0.01201 (7)	0.01201 (7)	0.01744 (11)	0	0	0
O	0.0173 (3)	0.0172 (3)	0.0265 (4)	0.0032 (3)	−0.0093 (3)	−0.0063 (4)

Geometric parameters (Å, °)

Rb—O	3.0890 (17)	Rb—Oⱽⁱⁱ	2.9304 (12)
Rb—Oⁱ	3.0890 (17)	As—O	1.6828 (11)
Rb—Oⁱⁱ	3.0890 (17)	As—Oⁱ	1.6828 (11)
Rb—Oⁱⁱⁱ	3.0890 (17)	As—Oⱽⁱⁱⁱ	1.6828 (11)
Rb—Oⁱᵛ	2.9304 (12)	As—Oⁱˣ	1.6828 (11)
Rb—Oᵛ	2.9304 (12)	O—H	0.850 (8)
Rb—Oᵛⁱ	2.9304 (12)		

O—Rb—O^{i}	52.94 (3)	O—As—O^{i}	109.80 (5)
O—Rb—O^{ii}	143.26 (3)	O—As—O^{viii}	109.31 (5)
O—Rb—O^{iii}	143.26 (3)	O—As—O^{ix}	109.31 (5)
O—Rb—O^{iv}	82.32 (3)	O^{i}—As—O^{viii}	109.31 (5)
O—Rb—O^{v}	133.06 (3)	O^{i}—As—O^{ix}	109.31 (5)
O—Rb—O^{vi}	67.05 (3)	O^{viii}—As—O^{ix}	109.80 (5)
O—Rb—O^{vii}	80.84 (3)		

Symmetry codes: (i) −x, −y, z; (ii) y, −x, −z+1; (iii) −y, x, −z+1; (iv) −x+1/2, y, −z+3/4; (v) x−1/2, −y, −z+3/4; (vi) −y, −x+1/2, z+1/4; (vii) y, x−1/2, z+1/4; (viii) y, −x, −z; (ix) −y, x, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O—H···O^{x}	0.850 (8)	1.665 (6)	2.5125 (13)	175 (6)

Symmetry code: (x) x, −y+1/2, −z+1/4.