

All the computations were made with FORTRAN programs written by the author for the KDC II.

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### The crystal structure of the ion exchanger zirconium bis(monohydrogen orthoarsenate) monohydrate.\*

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The crystal structure of the synthetic ion exchanger zirconium bis(monohydrogen orthoarsenate) monohydrate,  $Zr(HAsO_4)_2 \cdot H_2O$ , has been determined. The crystals are isomorphous with the monoclinic  $\alpha$ -zirconium phosphate and have cell dimensions  $a = 9.178(4)$ ,  $b = 5.378(2)$ ,  $c = 16.55(1)$  Å and  $\beta = 111.30(5)^\circ$ . The calculated density with  $Z = 4$  is  $3.395 \text{ g.cm}^{-3}$  compared with an observed density of  $3.3 \text{ g.cm}^{-3}$ . The structure was refined to an  $R$  value of 9.0% by the block-diagonal method. Anisotropic thermal parameters were obtained by refinement only on those reflections for which  $\sin^2 \theta \leq 0.35$ . The average zirconium-oxygen bond length is  $2.075$  Å ( $2.07$  Å in the phosphate). The arsenate groups deviate considerably from tetrahedral symmetry but the deviations are similar to those of the phosphate groups in  $\alpha$ -zirconium phosphate. The average arsenic-oxygen bond distance for non-hydrogen bearing (bridging) oxygen atoms is  $1.655$  Å. The cation sieving behavior of zirconium arsenate is discussed on the basis of its structure.

#### Introduction

The crystal structure of  $\alpha$ -zirconium bis(monohydrogen orthophosphate) monohydrate ( $\alpha$ -ZrP),  $Zr(HPO_4)_2 \cdot H_2O$ , has been determined as part of a fundamental study of synthetic, inorganic ion exchange compounds (Clearfield & Smith, 1969). Crystals isomorphous with this phosphate include the compounds commonly called titanium and hafnium phosphate and zirconium arsenate. All of these compounds, when crystalline, exhibit ion sieving behavior. In acid solutions titanium phosphate readily exchanges lithium and sodium ions, partially exchanges potassium ion and excludes rubidium and cesium ions (Alberti, Cardini-Galli, Constantino & Torracca, 1967).  $\alpha$ -ZrP crystals exchange lithium, sodium and potassium ions but exclude rubidium and cesium ions (Clearfield & Stynes, 1964) while zirconium arsenate exchanges with these ions and also partially exchanges rubidium but not cesium ions (Clearfield, Smith & Hammond, 1968; Torracca, Constantino & Massucci, 1967).

The structure of  $\alpha$ -ZrP is a layered one (Clearfield & Smith, 1969). The layers are arranged relative to one another in such a way as to create zeolite-like cavities within the crystal lattice. The initial stage of exchange involves diffusion of unhydrated or partially hydrated ions into the cavities (Clearfield, Duax, Medina, Smith & Thomas, 1969). Thus, the size of the entrances into the cavities apparently determines the size of the cations which can enter the lattice.

In  $\alpha$ -ZrP these are such as to permit a spherical ion of 2.64 Å diameter or smaller to pass. This size correlates well with the observed sieving behavior. It was therefore of interest in determining the structures of other isomorphous crystals to see whether the correlation persists. A further incentive for doing these structures was the possibility of locating the hydrogen atoms which were not determined in the zirconium phosphate structure.

This paper reports on the crystal structure of the isomorphous zirconium arsenate ( $\alpha$ -ZrAs).

#### Experimental

The preparation of microcrystals and their composition has been previously described (Clearfield, Smith & Hammond, 1968). Larger crystals suitable for X-ray diffraction studies were grown from the microcrystals by heating them at 150–160 °C in sealed tubes containing 1M arsenic acid and 6M nitric acid. The crystals were thin hexagonal platelets elongated parallel to the  $b$  axis.

The unit-cell dimensions were determined from a least-squares fit of back reflection Weissenberg data corrected for film shrinkage. The crystals are monoclinic with  $a = 9.178(4)$ ,  $b = 5.378(2)$ ,  $c = 16.55(1)$  Å,  $\beta = 111.30(5)^\circ$ . The values in parentheses represent the uncertainty in the last significant figure. This primitive cell is one-third the size of the previously reported cell (Clearfield, Smith & Hammond, 1968). The difference arises from the location of the  $c$  axis. In the previous work the direction of the reported  $c$  axis is actually that of  $c^*$ . The density was determined on a single crystal by the flotation method in diiodomethane, the liquid being slowly warmed until the crystal remained suspended. The value found was  $3.3 \text{ g.cm}^{-3}$ ; the calculated with  $Z = 4$  is  $3.395 \text{ g.cm}^{-3}$ .

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The systematic absences,  $h0l$  with  $l$  odd and  $0kl$  with  $k$  odd, restricted the space group to  $P2_1/c$ .

Intensity data were gathered on a Stoe integrating Weissenberg camera using nickel filtered copper radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Equi-inclination photographs were taken about the  $a$  axis,  $nkl$  ( $n=0-5$ ), and the  $b$  axis,  $hnl$  ( $n=0-3$ ) using the multiple-film technique. Intensities were read with a Joyce-Loebl integrating microdensitometer and Lorentz and polarization corrections were applied.

Two crystals of almost identical size and shape were used to gather the intensity data. They were thin rectangular platelets  $0.25 \text{ mm}$  wide by  $0.33 \text{ mm}$  long by  $0.091 \text{ mm}$  thick. The linear absorption coefficient for  $\text{Cu } K\alpha$  is  $23.77 \text{ cm}^{-1}$  and is high enough to introduce considerable error in the intensities because of the shape of the crystals. Therefore, an absorption correction was applied using a program, written in this laboratory by G. D. Smith, to deal with the case of crystals having the shape of thin platelets. After these corrections were applied the intensities were placed on the same scale using the least-squares procedure of Monahan, Shiffer & Shiffer (1967). Equivalent reflections were averaged and weights based upon standard deviations from the calculated mean were applied. In all 1025 non-zero, non-equivalent intensities were recorded.

#### Structure determination and refinement

The initial set of atomic parameters chosen were those of the isomorphous  $\alpha\text{-ZrP}$  structure. These were sufficiently accurate to permit least-squares refinement (block-diagonal method) to commence at once. The programs used were those of F. H. Ahmed *et al.*, as listed in Clearfield & Smith (1969). Atomic scattering factors for neutral atoms were taken from tabulations in *International Tables for X-ray Crystallography* (1962). The real part of the dispersion correction was applied to the zirconium and arsenic scattering curves. The function minimized in the least-squares program was  $W(|F_o| - |F_c|)^2$ .

After the first least-squares cycle it was evident that two of the oxygen atoms were out of place. These were given new parameters to accord more closely with the tetrahedral symmetry of the arsenate groups. Following this change the residual,  $R = \sum |F_o| - |F_c| / \sum |F_o|$ , was reduced to 0.12 in four cycles using isotropic thermal parameters. At this point anisotropic thermal parameters were introduced and refinement continued to a final  $R = 0.090$ . During these latter

cycles the unobserved reflections (500 in number) were given the minimum observed intensity and were only allowed to affect the refinement if the calculated intensity exceeded this minimum. At the end of the refinement the set of six thermal parameters for oxygen number 6 was not positive definite. Examination of the data showed that for 122 reflections  $\Delta F$  exceeded twice the reliability index. Of these, fifteen at low angles had low values of  $F_o$  and may have been subject to extinction errors. The majority of the remaining reflections were those most affected by absorption, *i.e.* those to which the highest absorption corrections had been applied. A third systematic error arises from the use of neutral atom scattering factors. Such factors are unable to duplicate the actual electron distribution resulting from the atoms being partially ionic and from localization of electrons due to covalent bonding. These errors would be greatest at low angles of diffraction.

In view of the above two additional refinements were carried out. In the first the 122 structure factors with largest residuals were eliminated. This necessitated re-evaluation of the individual scale factors for each film and remerging of the data to place them on the same relative scale. The refinement on this smaller body of data did not change the positional or thermal parameters within one standard deviation of those obtained by refinement on all data. However,  $R$  was reduced to 0.065.

Refinement was next carried out with data (741 reflections) for which  $\sin^2 \theta \geq 0.35$ . These data are the least affected

Table 1. Atomic parameters with estimated standard deviations\*

	X	Y	Z
Zr(1)	0.2401 (1)	0.7438 (2)	0.4857 (1)
As(2)	0.0032 (2)	0.7575 (3)	0.6144 (1)
As(3)	0.4684 (2)	0.2641 (3)	0.1036 (1)
O(4)	0.1204 (10)	0.8468 (21)	0.5646 (7)
O(5)	0.9455 (12)	0.4661 (19)	0.5953 (7)
O(6)	0.8515 (11)	0.9502 (16)	0.5923 (6)
O(7)	0.1054 (14)	0.7568 (21)	0.7231 (7)
O(8)	0.3180 (11)	0.0711 (19)	0.0592 (7)
O(9)	0.4287 (11)	0.5532 (19)	0.0687 (7)
O(10)	0.5152 (13)	0.2590 (19)	0.2129 (7)
O(11)	0.3731 (10)	0.8385 (18)	0.9105 (7)
O(12)	0.2541 (15)	0.2838 (30)	0.2626 (8)

\* Numbers in parentheses here and in succeeding Tables are estimated standard deviations in the least significant digits.

Table 2. Vibration tensor components and their e.s.  $d$ 's ( $\text{\AA}^2$ )†

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Zr	0.0162 (4)	0.0125 (5)	0.0313 (5)	0.0000 (4)	0.0006 (2)	0.0002 (4)
As(2)	0.0168 (5)	0.0158 (6)	0.0278 (5)	-0.0001 (4)	0.0005 (2)	0.0003 (4)
As(3)	0.0173 (6)	0.0131 (6)	0.0297 (5)	0.0002 (4)	0.0006 (2)	0.0003 (4)
O(4)	0.021 (4)	0.022 (4)	0.039 (5)	0.0006 (6)	0.0009 (3)	0.0009 (4)
O(5)	0.022 (4)	0.021 (4)	0.041 (5)	0.0000 (6)	0.0002 (2)	0.0004 (2)
O(6)	0.031 (5)	0.021 (4)	0.039 (5)	0.0009 (6)	0.0014 (4)	0.0009 (4)
O(7)	0.034 (5)	0.044 (7)	0.034 (5)	-0.0006 (6)	0.0011 (2)	0.0000 (4)
O(8)	0.028 (5)	0.020 (4)	0.042 (5)	-0.0008 (6)	0.0008 (2)	-0.0011 (5)
O(9)	0.021 (4)	0.026 (5)	0.035 (5)	0.0011 (6)	0.0004 (2)	0.0009 (4)
O(10)	0.034 (5)	0.027 (5)	0.036 (5)	-0.0001 (6)	0.0007 (2)	0.0001 (4)
O(11)	0.014 (3)	0.015 (4)	0.047 (5)	0.0004 (6)	0.0009 (2)	0.0010 (4)
O(12) water	0.045 (7)	0.064 (10)	0.041 (5)	-0.0002 (6)	0.0009 (2)	-0.0024 (8)

† Thermal parameters are in the form

$$\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)]$$

where  $B_{11} = 2\pi^2 a^{*2} U_{11}$ , etc.

$$B_{13} = 4\pi^2 a^* c^* U_{13}, \text{ etc.}$$

Table 3. Observed and calculated structure factors x 10 (in electrons) for alpha-Zr As\*

Table with columns for h, k, l, Fo, Fc, and multiple columns for different reflections. The table lists observed (Fo) and calculated (Fc) structure factors for various reflections. Asterisks denote unobserved reflections.

\* Asterisks denote unobserved reflections.

by extinction and errors due to the use of neutral atom scattering factors. The positional parameters did not change by more than two standard deviations over the previous refinements. However, the thermal parameters changed (increased) by as much as 40% while the scale factor was lowered by 14%. The sets of  $\beta_{ij}$  values were now positive definite for all atoms. The final  $R$  for the upper angle data was 0.075.

Several weighting schemes were tried including one based upon the weights calculated from the standard deviations from the mean of the measured film data. In all cases the positional and thermal parameters were insensitive to the weighting scheme used. The one finally adopted was  $\sqrt{W}=1$  when  $|F_o| \leq P_1$  and  $\sqrt{W}=P_1/|F_o|$  when  $|F_o| > P_1$ , where  $P_1=6.0$ .

The positional parameters listed in Table 1 and the structure factors in Table 3 are those obtained by refinement of all the data. However, the thermal parameters in Table 2 are those obtained from refinement on upper angle data only. These were referred to an orthogonal axial system by making  $c$  perpendicular to the  $ab$  plane. The final difference map showed several positive regions of height about 10% that of an oxygen atom. These peaks could not be assigned to hydrogen atoms since they gave unreasonable bond distances or failed to refine. Thus, the positive regions must arise from other causes, primarily series termination effects and the systematic errors discussed above.

### Results and discussion

The structure of  $\alpha$ -ZrAs is essentially that described earlier for  $\alpha$ -ZrP (Clearfield & Smith, 1969). Tables 4 and 5 present a comparison of the bond distances and angles in the isomorphous phosphate and arsenate. The standard deviations given are those based on random errors. However, the several refinements carried out for the arsenate yielded bond distances which differed by as much as 0.02 Å. Thus, standard deviations of approximately twice those listed in the Tables would be a more reliable indicator of the accuracy of the data.

The deviations from tetrahedral symmetry of the arsenate groups are quite similar to those exhibited by the phosphate groups. Since the phosphate data were obtained by the precession method with Mo  $K\alpha$  radiation and the arsenate by the Weissenberg method with Cu  $K\alpha$  radiation, the reported deviations would appear to be real. These distortions probably arise from the stringent spatial requirements for

Table 5. Bond angles in degrees

	Phosphate	Arsenate
O(4)-Zr-O(5)	91.2 (9)°	93.1 (4)°
O(4)-Zr-O(6)	88.3 (8)	89.6 (4)
O(4)-Zr-O(8)	90.3 (9)	89.9 (4)
O(4)-Zr-O(9)	90.2 (8)	89.9 (4)
O(4)-Zr-O(11)	179.9 (8)	175.6 (4)
O(4)-As(2) [P(2)]-O(5)	113.8 (14)	113.8 (5)
O(4)-As(2)-O(6)	109.5 (13)	110.8 (5)
O(4)-As(2)-O(7)	109.8 (15)	108.7 (5)
O(5)-As(2)-O(6)	110.2 (14)	111.4 (5)
O(5)-As(2)-O(7)	102.6 (16)	102.5 (5)
O(6)-As(2)-O(7)	110.8 (15)	109.2 (5)
O(8)-As(3) [P(3)]-O(9)	112.1 (14)	112.9 (5)
O(8)-As(3)-O(10)	110.1 (16)	107.9 (5)
O(8)-As(3)-O(11)	111.1 (14)	111.1 (5)
O(9)-As(3)-O(10)	107.5 (15)	108.9 (5)
O(9)-As(3)-O(11)	109.7 (13)	111.0 (5)
O(10)-As(3)-O(11)	106.0 (15)	104.4 (5)

bridging of 3 metal atoms by each  $\text{MO}_4^{2-}$  group. Similar distortions occur in the  $\text{MgHPO}_4$  structure (Sutor, 1967).

The average zirconium-oxygen bond length is the same in both structures. The average arsenic-oxygen bond length for the bridging oxygen atoms, 1.655(10), is somewhat shorter than the 1.701(11) found for the hydrogen-bearing oxygen atoms. These bond lengths are considerably shorter than those found in  $\text{Ag}_3\text{AsO}_4$ , average 1.75 Å, and  $\text{KH}_2\text{AsO}_4$ , average 1.74 Å, (Helmholtz & Levine, 1942) but agree more closely with those found in  $\text{Cu}_3(\text{AsO}_4)_2$ , average 1.69 Å, (Poulsen & Calvo, 1968) and  $\text{Mg}_2\text{As}_2\text{O}_7$ , average 1.67 Å (Lukasiewicz, 1966).

As already mentioned the hydrogen atom positions were not obtained. The high thermal motion parallel to the layers exhibited by the water molecule and the hydrogen bearing oxygen atoms O(7) and O(10) is partly responsible for the inability to locate the hydrogen atoms. This thermal motion is reasonable since these atoms are the ones least constrained by bonding. Thus, the hydrogen bonds must be inferred from oxygen-oxygen interatomic distances. These are listed in Table 6. Two possible hydrogen bonding schemes were described earlier (Clearfield & Smith, 1969). The arsenate data do not allow a choice between the two schemes. The resolution of this problem must await the outcome of a neutron diffraction study.

Table 6. Possible hydrogen bond distances\*

Interatomic distance	Phosphate	Arsenate
O(12)-O(7)	3.06 (6) Å	3.18 (2) Å
O(12)-O(7')	2.82 (6)	2.78 (2)
O(12)-O(10)	2.78 (3)	2.80 (2)
O(12)-O(11)	3.22 (6)	3.06 (2)
O(10'')-O(10)	3.07 (6)	3.01 (2)
O(10'')-O(10')	3.07 (6)	3.01 (2)

\* Primed atoms are as in Fig. 5 of Clearfield & Smith (1969).

Table 4. Bond distances in zirconium phosphate and arsenate

	Phosphate	Arsenate
Zr-O(4)	2.04 (2) Å	2.064 (10) Å
Zr-O(5)	2.08 (2)	2.077 (11)
Zr-O(6)	2.06 (2)	2.072 (9)
Zr-O(8)	2.05 (2)	2.055 (10)
Zr-O(9)	2.12 (2)	2.085 (10)
Zr-O(11)	2.06 (2)	2.083 (10)
	Avg. 2.07	2.073
[P(2)] As <sub>2</sub> -O(4)	1.51 (2)	1.646 (10)
As <sub>2</sub> -O(5)	1.51 (3)	1.648 (10)
As <sub>2</sub> -O(6)	1.51 (2)	1.666 (11)
As <sub>2</sub> -O(7)	1.60 (2)	1.700 (11)
[P(3)] As <sub>3</sub> -O(11)	1.54 (2)	1.650 (10)
As <sub>3</sub> -O(9)	1.50 (3)	1.652 (10)
As <sub>3</sub> -O(8)	1.51 (3)	1.669 (10)
As <sub>3</sub> -O(10)	1.54 (2)	1.702 (11)

Calculation of the interatomic distances between atoms forming the cavity in zirconium arsenate was carried out in the same manner as was previously done for  $\alpha$ -zirconium phosphate (Clearfield, Duax, Medina, Smith & Thomas, 1969). This analysis shows that the largest free volume is such as to allow a spherical ion of 2.57 Å, compared with 2.62-4 Å for phosphate, to pass freely into the cavity. This is just slightly smaller than the size of an unhydrated po-

tassium ion. Thus, it is to be expected that rubidium ion would not exchange unless swelling of the crystals occurred in the presence of rubidium ion. This point is being investigated and will be reported on subsequently.

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**The crystal and molecular structure of 2-bromo-*N*-salicylideneaniline.** By A. H. BURR and A. D. HOBSON\*,  
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$C_6H_4(OH)CH=NC_6H_4Br$  crystallizes in the orthorhombic space group  $P2_12_12_1$  with lattice constants  $a=12.30(4)$ ,  $b=7.09(2)$  and  $c=13.44(4)$  Å. The crystals are photochromic; the mechanism of the photo-reversible change has been attributed to the shift of the hydroxylic hydrogen atom to the nitrogen atom of one molecule. The molecular configuration verifies the existence of intramolecular hydrogen bonding and the packing is of the same type as in other *N*-salicylideneanilines whose structures are known.

### Introduction

It has been shown by earlier workers (Cohen, Hirshberg & Schmidt, 1959) that when the pale yellow crystals of anil are irradiated with near ultraviolet wavelengths an induced absorption band is produced. This corresponds to a deepening in colour of the anil crystals to orange-red. The original colour may be restored by keeping the crystals in the dark for some time, by heating them (thermal bleaching) or by exposing them to visible light (optical bleaching).

Various theories have been proposed to explain the photochromic mechanism in anils but all of the more recent ones (Cohen *et al.*, 1959; Cohen & Schmidt, 1962; Wettermark & Dogliotti, 1964; Anderson & Wettermark, 1965; Dudek & Dudek, 1966; Ledbetter, 1966; Becker & Richey, 1967) stress the importance of an enol-keto tautomerism caused by the intramolecular movement of the hydroxylic hydrogen atom to the azomethine nitrogen atom promoted by the activating radiation. The structural requirements for this mechanism in 2-bromo-*N*-salicylideneaniline were investigated by X-ray analysis.

### Experimental

2-Bromo-*N*-salicylideneaniline was prepared by condensing salicylaldehyde with *o*-bromoaniline. Recrystallization from absolute ethanol produced pale yellow crystals melting at 86°C and having a measured density of  $1.56 \pm 0.01$  g.cm<sup>-3</sup>.

Larger crystals were tabular in habit, exhibiting form {110}. X-ray examination confirmed that the compound was orthorhombic;  $a=12.30(4)$ ,  $b=7.09(2)$ ,  $c=13.44(4)$  Å. Further, systematic absences of reflexions  $h00$ ,  $0k0$  and  $00l$  for  $h$ ,  $k$  or  $l$  odd were noted, indicating space group  $P2_12_12_1$ . Hence, the assumption that the unit cell contains 4 molecules (occupying general positions) gives a calculated density of 1.60 g.cm<sup>-3</sup>.

A crystal was selected for intensity measurements and shaped into an approximate cube of side 90μ. It was mounted on a Weissenberg goniometer and zero-layer photographs were obtained with the crystal rotating first about the  $y$  axis and then about the  $x$  axis. The multiple-film technique (involving 2 packs of 4 films each) was used, with Cu  $K\alpha$  radiation. Observed intensities of 324 reflexions were acquired by visual estimation using a prepared intensity scale. Intensity values were corrected for Lorentz and polarization factors; absorption corrections were neglected on the grounds that the use of such a small crystal had made their application unnecessary. The observed intensities were put on an approximately absolute scale by employing a scaling factor derived by the Wilson (1942) method.

### Structure determination

The presence of the relatively heavy bromine atoms facilitated the interpretation of two-dimensional Patterson vector maps which were computed from the observed intensities. From projections along [100] and [010] coordinates were deduced for the bromine general position and thence a preliminary set of structure factors was calculated, based on the bromine position only. From these structure factors

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