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Metavariscite – A Redetermination of its Crystal Structure

BY RÜDIGER KNIEP* AND DIETRICH MOOTZ*

Institut für Anorganische Chemie der Technischen Universität Braunschweig, 33 Braunschweig, Pockelsstrasse 4 Germany (BRD)

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Abstract. Metavariscite, $AlPO_4.2H_2O$, monoclinic, $P2_1/n$, $a=5{\cdot}178$ (2), $b=9{\cdot}514$ (2), $c=8{\cdot}454$ (2) Å, $\beta=90{\cdot}35$ (2)°, $Z=4$, $D_m=2{\cdot}54$, $D_x=2{\cdot}535$ g cm^{-3}. Material from Utalith Hill, Lucin, Utah, U.S.A.† PO_4 tetrahedra share vertices with four $AlO_4(OH_2)_2$ octahedra and *vice versa*. With Al$\cdots$O distances of 1·892 (2) and 1·953 (2) Å the two waters coordinate the aluminum in *cis*-position and donate two single and quite short and two bifurcated longer hydrogen bonds, respectively, to phosphate oxygens. None of the hydrogen bonds is along an octahedron edge.

Introduction. Cell constants were determined from diffractometric measurements. The systematic absences are $h0l$ for $h+l$ odd and $0k0$ for k odd. The intensities of 1215 independent reflexions with $\theta \le 30°$ were measured with Zr-filtered Mo $K\alpha$ radiation on a tape-controlled Siemens automatic diffractometer with $\theta/2\theta$ scan.

The crystal size was approximately $0{\cdot}3\times0{\cdot}3\times0{\cdot}2$ mm. 1067 reflexions had significant intensities. No correction for absorption ($\mu=8{\cdot}2$ cm^{-1}) was applied. Least-squares refinement on F was started from non-hydrogen atom parameters reported by Borensztajn (1966). The four hydrogen atoms could easily be located as the highest peaks in a difference map. The final R was 0·027 for all reflexions (0·023 for significant reflexions only).

The form factors used were those of Hanson, Herman, Lea & Skillman (1964) for P, Al and O, and of Stewart, Davidson & Simpson (1965) for H. The observations were weighted according to $w=1/\sigma_F^2$ with σ_F evaluated from the measurements.

* Present address: Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 1, Heilbronnerstrasse 69, Germany (BRD). The paper is a shortened part of the 'Diplomarbeit' in mineralogy of R. K. (Kniep, 1971).

† The sample (National Museum of Natural History catalog number 113753) was kindly provided by Mr John S. White Jr, Museum Specialist at the Smithsonian Institution, Division of Mineralogy, Washington D.C., U.S.A.

Table 1. *The atomic parameters and their standard deviations*

The B_{ij} in Å^2 are listed using the expression $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+2B_{23}klb^*c^*+\ldots)]$. Hydrogen atoms were refined anisotropically because a mixed-mode program was not available.

	x	y	z
Al	0·40309 (9)	0·32545 (5)	0·30626 (5)
P	−0·09105 (8)	0·14688 (4)	0·18371 (4)
O(1)	0·16505 (22)	0·17902 (11)	0·27036 (13)
O(2)	−0·09291 (23)	0·21677 (12)	0·02094 (13)
O(3)	−0·31481 (22)	0·20439 (12)	0·28127 (13)
O(4)	−0·11458 (21)	−0·01392 (11)	0·17227 (13)
O(*W*1)	0·11617 (30)	0·44767 (15)	0·32202 (18)
O(*W*2)	0·40410 (31)	0·36239 (14)	0·07903 (15)
H(11)	0·139 (5)	0·530 (3)	0·288 (4)
H(12)	−0·037 (7)	0·432 (3)	0·331 (5)
H(21)	0·274 (7)	0·334 (5)	0·023 (4)
H(22)	0·539 (8)	0·369 (5)	0·023 (4)

Table 1 (*cont.*)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	0·38 (2)	0·48 (1)	0·34 (1)	−0·00 (6)	0·00 (1)	0·01 (1)
P	0·32 (1)	0·38 (1)	0·27 (1)	0·01 (1)	0·00 (1)	−0·02 (1)
O(1)	0·60 (4)	0·74 (4)	0·93 (4)	−0·06 (3)	−0·23 (3)	−0·06 (3)
O(2)	1·27 (5)	0·83 (4)	0·44 (4)	0·00 (2)	0·07 (3)	0·07 (3)
O(3)	0·69 (4)	1·01 (4)	0·69 (4)	0·24 (3)	0·22 (3)	−0·04 (3)
O(4)	0·60 (4)	0·49 (4)	0·90 (4)	−0·01 (2)	−0·08 (3)	−0·03 (3)
O(*W*1)	0·57 (5)	0·80 (5)	2·59 (6)	0·03 (3)	0·16 (4)	0·31 (4)
O(*W*2)	1·45 (5)	1·59 (5)	0·61 (4)	−0·30 (4)	−0·14 (4)	−0·02 (7)
H(11)	1·5 (1·3)	0·7 (1·0)	4·3 (1·7)	−0·6 (0·9)	−0·4 (1·4)	0·6 (1·3)
H(12)	1·5 (1·5)	4·0 (1·8)	7·1 (2·3)	2·4 (1·4)	−1·6 (1·6)	−0·0 (0·5)
H(21)	2·5 (1·8)	15·3 (4·0)	1·7 (1·4)	3·7 (1·9)	1·9 (1·3)	4·5 (1·9)
H(22)	5·8 (2·5)	17·5 (3·6)	1·4 (1·4)	9·3 (2·5)	1·1 (1·7)	2·3 (2·0)

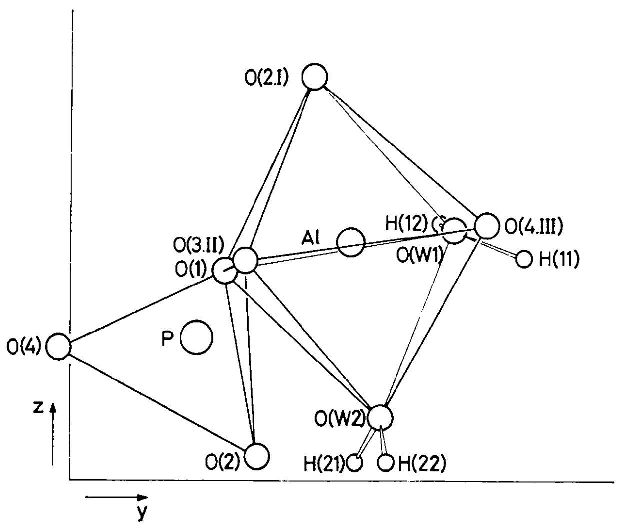

Fig. 1. The $AlO_4(OH_2)_2$ octahedron and the PO_4 tetrahedron of the metavariscite crystal structure.

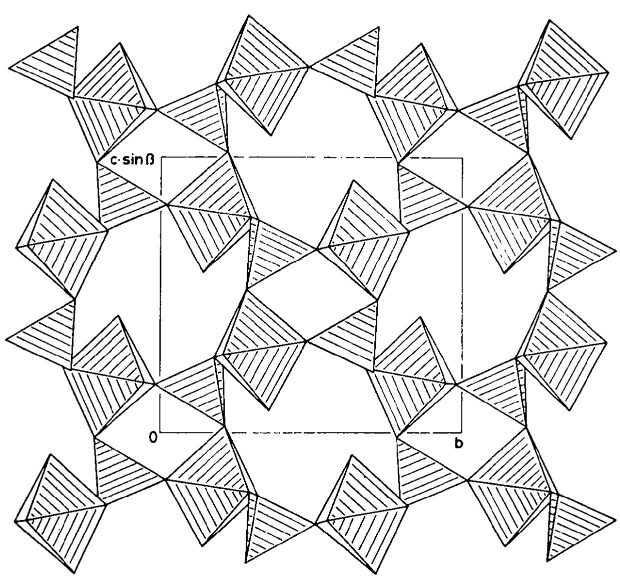

Fig. 2. Linking of the $AlO_4(OH_2)_2$ octahedra and PO_4 tetrahedra through common vertices. Translation of the net shown along the short *a* axis generates a three-dimensional framework.

The atomic coordinates and thermal parameters are given in Table 1. A table of observed and calculated structure factors is available.*

Discussion. An earlier determination and isotropic refinement of the structure from 650 eye-estimated photographic Cu *Kα* intensities yielded the heavy-atom positions only (Borensztajn, 1966). *R* was 0·16 and the estimated standard deviations of interatomic distances were in the range 0·02 to 0·03 Å. This redetermination is part of a systematic study of crystal structures and genetic principles of alumina phosphate hydrate minerals (Kniep, 1971; Kniep, Schumann & Mootz, 1972). There is a special interest in these compounds because of their varying water content and different water

* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30149 (8pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Lengths and angles of covalent and ionic bonds*

The estimated standard errors are in the range 0·001 to 0·002 Å and 0·1 to 0·2°.

P–O(1)	1·542 Å	O(1)–P–O(2)	110·0°
P–O(2)	1·528	O(1)–P–O(3)	108·9
P–O(3)	1·528	O(1)–P–O(4)	107·1
P–O(4)	1·538	O(2)–P–O(3)	109·2
		O(2)–P–O(4)	112·1
		O(3)–P–O(4)	109·2
Al–O(1)	1·883 Å	O(1)—Al–O(2)	90·0°
Al–O(2,I)	1·859	O(1)—Al–O(3)	92·1
Al–O(3,II)	1·873	O(1)—Al–O(4)	173·0
Al–O(4,III)	1·888	O(1)—Al–O(*W*1)	87·2
Al–O(*W*1)	1·892	O(1)—Al–O(*W*2)	88·8
Al–O(*W*2)	1·953	O(2)—Al–O(3)	88·4
		O(2)—Al–O(4)	94·4
O(*W*1)–H(11)	0·84 Å	O(2)—Al–O(*W*1)	93·9
O(*W*1)–H(12)	0·81	O(2)—Al–O(*W*2)	177·7
O(*W*2)–H(21)	0·87	O(3)—Al–O(4)	93·2
O(*W*2)–H(22)	0·85	O(3)—Al–O(*W*1)	177·5
		O(3)—Al–O(*W*2)	89·6
		O(4)—Al–O(*W*1)	87·1
		O(4)—Al–O(*W*2)	86·7
		O(*W*1)–Al–O(*W*2)	88·0
I: $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$			
II: $1+x, y, z$		H(11)–O(*W*1)–H(12)	110°
III: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$		H(21)–O(*W*2)–H(22)	111

Table 3. *The geometry of hydrogen bonds and other short* O(*W*)···O *contacts*

Listed are all d[O(W)···O] smaller than 3·0 Å. The estimated standard errors are 0·002 Å for d[O(W)···O], 0·03 Å for d[H(a/b)···O], and 2° for angle at H(a/b). Values characteristic for hydrogen bonds (two single from O(W1) and two bifurcated from O(W2)) are marked with an asterisk. All remaining O(W)···O contacts are edges of the $AlO_4(OH_2)_2$ octahedron.

I :	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
II:	$1+x$,	y,	z
III:	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
IV:	$-\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
V:	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$

O(W)—H(a/b)·····O		d[O(W)···O]	d[H(a/b)···O]		Angle at H	
			a	b	a	b
O(W1)–H(11/12)···	O(1)	2·605 Å	3·35 Å	2·68 Å	25°	76°
	O(1,III)	2·598*	1·81*	3·16	154*	41
	O(2,I)	2·741	3·36	3·14	38	54
	O(4,IV)	2·623*	2·77	1·88*	71	153*
	O(4,III)	2·607	2·52	3·41	87	7
	O(W2)	2·672	2·75	3·20	76	43
O(W2)–H(21/22)···	O(1)	2·686 Å	2·62 Å	3·38 Å	85°	31°
	O(1,V)	2·972*	2·95	2·28*	83	139*
	O(2,II)	2·993*	3·46	2·39*	51	128*
	O(2)	2·961*	2·20*	3·50	146*	45
	O(3,II)	2·696	3·28	2·79	42	75
	O(3,V)	2·827*	2·12*	2·82	138*	82
	O(4,III)	2·639	3·44	2·84	20	68
	O(W1)	2·672	2·87	3·44	68	22

species (H_2O, OH^- and possibly H_3O^+) along with the same recurrent building units of cation and anion polyhedra.

Bond lengths and bond angles are listed in Table 2. Table 3 gives the geometry of hydrogen bonds and other short O(W)···O contacts. Fig. 1 shows the asymmetric unit plus some more symmetry-equivalent atoms, necessary to generate a complete $AlO_4(H_2O)_2$ octahedron besides the PO_4 tetrahedron. Fig. 2 shows the repetition of this unit of structure into a three-dimensional framework.

Despite the highly significant difference of the two Al···O(W) distances of 1·892 and 1·953 Å, both water molecules of the structure are true H_2O species. Their hydrogen bonding can be described in terms of two single (W1) and two bifurcated (W2) hydrogen bonds, none of which is to an oxygen atom of the same $AlO_4(OH_2)_2$ octahedron.

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Li_2ZrF_6

BY GEORGE BRUNTON

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *U.S.A.*

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Abstract. Hexagonal, $P\overline{3}1m$, $a_o=4{\cdot}9733$ (9), $c_o=4{\cdot}658$ (1) Å, 24·5°C, $Z=1$, $\varrho_x=3{\cdot}646$ g cm^{-3}. Six (Zr–F) at 2·016 (1) Å; 6(Li–F) at 2·0246 (9) Å. Each ZrF_6^{2-} ion is coordinated by $12Li^+$ ions; Zr–Li = 3·6971 (5) Å. Automated diffractometer data, 2θ scan, Si–Li detector, Mo $K\alpha$ radiation.

Introduction. The crystal structure of Li_2ZrF_6 was partially determined by Hoppe & Dahne (1960) with some ambiguity as to the position of the Li ions. This structural determination resolves that ambiguity and presents more precise structural parameters.

A crystal of Li_2ZrF_6 grown from a melt of the stoi-