

## The structure of $\text{Ba}_3(\text{VO}_4)_2$

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### Auszug

ZACHARIASEN bestimmte die Strukturen von  $\text{Sr}_3(\text{PO}_4)_2$  und  $\text{Ba}_3(\text{PO}_4)_2$  aus Pulveraufnahmen; später fand DURIF ebenfalls mittels der Pulvermethode die gleiche Struktur bei einigen ähnlichen Verbindungen. Unsere Untersuchung wurde an einer kleinen, aus einem nach CZOCHRALSKIS Methode gezüchteten Kristall geschliffenen Kugel von  $\text{Ba}_3(\text{VO}_4)_2$  durchgeführt. Präzessionsaufnahmen ergaben eine Interferenzsymmetrie, die mit der von ZACHARIASEN gefundenen Raumgruppe  $R\bar{3}2/m$  übereinstimmt. Die Gitterkonstanten in hexagonaler Aufstellung sind:  $a = 5,762 \text{ \AA}$ ,  $c = 21,29 \text{ \AA}$ . Die Intensitäten wurden mit einem voll-automatischen Vierkreis-Diffraktometer gemessen. Bei der Verfeinerung wurde von den von ZACHARIASEN angegebenen Atomkoordinaten ausgegangen;  $R$  fiel durch die Verfeinerung von 22% auf 4,8%. Die Struktur ist anscheinend bisher nicht diskutiert worden. Das Vanadium ist tetraedrisch von Sauerstoff umgeben. Das Ba-Atom kommt in zwei Koordinationen vor: in einer deformiert-oktaedrischen und in einer Zehner-Umgebung. Drei Ba-Atome, Ba(2), Ba(1), Ba(2), bilden einen linearen Verbund, in dem aufeinanderfolgende Ba-Atome gemeinsame dreieckige Flächen ihrer Koordinations-Polyeder haben. Auch bei den Sauerstoffatomen gibt es zwei verschiedene Koordinationen: die einen O-Atome werden von zwei Metallatomen in diametral entgegengesetzten Lagen umgeben, die anderen von fünf Metallatomen in deformierten trigonalen Bipyramiden. PAULINGS Elektrostatische-Valenz-Regel ist vollkommen erfüllt; nur einige Bindungen sind unerwartet stark.

### Abstract

ZACHARIASEN determined the structures of  $\text{Sr}_3(\text{PO}_4)_2$  and  $\text{Ba}_3(\text{PO}_4)_2$  by the powder method. Later DURIF assigned other similar compounds to the same structure on the basis of powder photographs. Our investigation of  $\text{Ba}_3(\text{VO}_4)_2$  was made on a small spherical specimen ground from a single crystal grown by the Czochralski method. Precession photographs revealed a diffraction symmetry consistent with ZACHARIASEN's  $R\bar{3}2/m$  with  $a = 5.762$ ,  $c = 21.29 \text{ \AA}$ , referred to a hexagonal cell. Reflection intensities were measured with a fully automated four-circle diffractometer. Using ZACHARIASEN's coordinates for

$\text{Ba}_3(\text{PO}_4)_2$ , the  $R$  value started at 22% and was refined by least squares to 4.8%. The structure has apparently not been discussed previously. The vanadium is tetrahedrally surrounded by oxygen atoms. There are two kinds of barium atoms, one with distorted octahedral coordination, one with ten-fold coordination. Pairs of three barium atoms, Ba(2), Ba(1), Ba(2), share a common triangular face of their respective coordination polyhedra; these three thus form a connected linear cluster. There are two kinds of oxygen atoms; one has two-fold linear coordination, the other, five-fold trigonal-dipyramidal coordination. PAULING's electrostatic-valence rule is perfectly satisfied but some of the bond strengths are unexpected.

### Introduction

Most of the alkaline-earth phosphates, arsenates and vanadates have been referred to the structure assigned to  $\text{Sr}_3(\text{PO}_4)_2$  and  $\text{Ba}_3(\text{PO}_4)_2$  by ZACHARIASEN<sup>1</sup>, who based his determination of these trigonal structures upon powder data; the referring of other analogous compounds to the same structure type was also based upon powder data<sup>2</sup>.

On the other hand, when single crystals of  $\text{Ca}_3(\text{VO}_4)_2$  were examined by the precession method, it became clear that this compound has a different<sup>3</sup>, possibly related, crystal structure for, although trigonal, it has a multiple cell and different symmetry. In the program of establishing this more complicated structure it appeared desirable to confirm the simpler Zachariassen structure, which was established on the basis of qualitative estimates of powder-line intensities.

We were fortunate in enlisting the interest of Dr. LOTHAR BRIXNER (of the Central Research Laboratory, E. I. du Pont de Nemours, Wilmington, Delaware). Dr. BRIXNER attempted to grow the crystals of this group by the Czochralski method, and succeeded in producing single crystals of  $\text{Sr}_3(\text{VO}_4)_2$  and  $\text{Ba}_3(\text{VO}_4)_2$ . The experimental work made it evident that the other members of the group are most difficult to obtain in single-crystal form, and Dr. BRIXNER was unsuccessful in growing such material.

Of the two compounds which yielded single crystals,  $\text{Ba}_3(\text{VO}_4)_2$  was chosen for the purpose of checking the Zachariassen structure by single-crystal methods.

<sup>1</sup> W. H. ZACHARIASEN, The crystal structure of the normal orthophosphates of barium and strontium. *Acta Crystallogr.* **1** (1948) 263–265.

<sup>2</sup> ANDRÉ DURIF, Structure cristalline des orthovanadates et orthoarseniates de baryum et de strontium. *Acta Crystallogr.* **12** (1959) 420–421.

<sup>3</sup> MARTHA J. REDDEN and MARTIN J. BUEGER, Note on the symmetry and cell of calcium orthovanadate. *Z. Kristallogr.* **129** (1969) 459–460.

## Crystallographic data

The space group and cell were studied by the precession method. The diffraction symbol is  $\bar{3} \frac{2}{m} R3 -$ , implying space group  $R32$ ,  $R3m$  or  $R\bar{3} \frac{2}{m}$ . The refinement eventually confirmed the latter symmetry, which is the same as that given by ZACHARIASEN for Sr<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and by DURIF<sup>2</sup> for other members of this family of crystals. The cell dimensions are given in Table 1.

Table 1. Cell data for Ba<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>

Coordinate system	Parameter	This work	DURIF <sup>2</sup>
Rhombohedral	<i>a</i>	7.837 ± 0.009 Å	7.859 Å
	<i>α</i>	43.14 ± 0.4°	43° 10'
	<i>V</i>	204.1 Å <sup>3</sup>	206.0 Å <sup>3</sup>
	<i>Z</i>	1 formula unit	1
Hexagonal	<i>a</i>	5.762 ± .008 Å	5.783 Å
	<i>c</i>	21.29 ± .03 Å	21.34 Å
	<i>V</i>	612.3 Å <sup>3</sup>	618.0 Å <sup>3</sup>
	<i>Z</i>	3 formula units	3
	<i>ρ</i> <sub>cal</sub>	5.20 g/cm <sup>3</sup>	5.142 g/cm <sup>3</sup>

## Intensity measurement

A number of spheres were ground from the crystal, using the hydraulic sphere grinder developed in Dr. KARL FISCHER's laboratory at Saarbrücken; a sphere having a radius of 0.018 cm was selected for intensity measurement. A Picker 4-circle automated diffractometer and graphite-monochromated MoK $\alpha$  radiation were used for this purpose. The 1136 reflections in the hemisphere out to  $(\sin \theta)/\lambda = 0.63 \text{ \AA}^{-1}$  were measured.

These raw intensity data were corrected for Lorentz, polarization and absorption effects. To test the quality of the data, the differences of the intensities of sets of three reflections related by the three-fold axis were used to compute an amplitude discrepancy  $R_A$ , as follows

$$R_A = \frac{\sum (\Delta F_{12} + \Delta F_{23} + \Delta F_{31})}{\sum |F|} \quad (1)$$

there  $\Delta F_{12}$  is  $\|F_1| - |F_2\|$  of a pair of the three equivalent reflections, etc.

For the 1136 reflections of Ba<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>,  $R_A$  was 3.2%, a value which is consistent with that found by BERNHARDT WUENSCH<sup>4</sup> for tetrahedrite.

<sup>4</sup> BERNHARDT J. WUENSCH, The reliability of equi-inclination counter-diffractometer data. Acta Crystallogr. **16** (1963) 1259.

## Structure refinement

In beginning the determination of the structure of  $\text{Ba}_3(\text{VO}_4)_2$  it was most reasonable to assume DURIF's assignment of this crystal to ZACHARIASEN's structure type to be correct. Accordingly ZACHARIASEN's coordinates for  $\text{Ba}_3(\text{PO}_4)_2$ , and an overall isotropic  $B$  of  $0.80 \text{ \AA}^2$  were assumed to compute expected amplitudes. This yielded an  $R$  value of 22%, which generally confirmed ZACHARIASEN's (1948) structure determination for the members of this family of crystals.

Four cycles of least-squares refinement with individual isotropic temperature factors reduced  $R$  to 7.7%. Some 13 of the strongest reflections (for which  $|F_c|$ , as refined, was considerably greater than  $|F_o|$ ) were then eliminated, along with their symmetry equivalents; this elimination reduced  $R$  to 6.7%.

Five more cycles of least-squares refinement employing anisotropic temperature factors yielded an  $R$  value of 4.8%. The atomic parameters at this stage are given in Tables 2, 3 and 4. Table 5 gives the observed and computed amplitudes of the reflections; these are arranged so that one line contains the several  $F_o$ 's of symmetry-equivalent reflections, the average value of these equivalent  $F_o$ 's, and, for comparisons, the common  $F_c$ . The reflections omitted from the refinement are marked by an asterisk.

Table 2. Positional parameters of atoms in the  $\text{Ba}_3(\text{VO}_4)_2$  structure  
Rhombohedral description (obverse setting)

Atom	Equipoint	Coordinates	Positional parameters			
			$x$	$\sigma(x)$	$z$	$\sigma(z)$
Ba(1)	1a	000	—	—	—	—
Ba(2)	2c	xxx	.20525	.00002	—	—
V	2c	xxx	.40758	.00007	—	—
O(1)	2c	xxx	.3278	.0004	—	—
O(2)	6h	xxz	.2735	.0003	.7566	.0004

## Hexagonal description

Atom	Equipoint	Coordinates	Positional parameters			
			$x$	$\sigma(x)$	$z$	$\sigma(z)$
Ba(1)	3a	000	—	—	—	—
Ba(2)	6c	00z	—	—	.20525	.00002
V	6c	00z	—	—	.40758	.00007
O(1)	6c	00z	—	—	.3278	.0004
O(2)	18h	x $\bar{x}$ z	.1610	.0004	.5654	.0005

Table 3. *Thermal parameters of atoms in Ba<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>*  
 Temperature coefficients,  $B_{ij}$ , of  $e^{-\frac{1}{2}(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)}$   
 Rhombohedral description (obverse setting)

Atom	$B_{11}$	$\sigma(B_{11})$	$B_{22} = B_{11}$	$B_{33}$	$\sigma(B_{33})$	$B_{12}$	$\sigma(B_{12})$	$B_{13}$	$\sigma(B_{13})$	$B_{23}$	Equivalent isotropic $B$	$\sigma(B)$
Ba(1)	1.57 Å <sup>2</sup>	0.02 Å <sup>2</sup>		$= B_{11}$		-0.72 Å	0.01 Å <sup>2</sup>	$= B_{12}$	$= B_{12}$	$= B_{12}$	1.65 Å <sup>2</sup>	0.05 Å <sup>2</sup>
Ba(2)	0.95	0.01		$= B_{11}$		-0.41	0.01	$= B_{12}$	$= B_{12}$	$= B_{12}$	0.96	0.03
V	1.34	0.03		$= B_{11}$		-0.63	0.02	$= B_{12}$	$= B_{12}$	$= B_{12}$	1.42	0.08
O(1)	2.4	0.2		$= B_{11}$		-1.1	0.1	$= B_{12}$	$= B_{12}$	$= B_{12}$	2.5	0.4
O(2)	1.0	0.1		0.9 Å <sup>2</sup>	0.1 Å <sup>2</sup>	-0.5	0.1	-0.4 Å <sup>2</sup>	0.1 Å <sup>2</sup>	$= B_{13}$	1.0	0.3

Table 4. *Parameters for the ellipsoids of vibration*

Atom	Root-mean-square amplitude along the principal axes	Angles with axes of hexagonal cell		
		$a_1$	$a_2$	$c$
Ba(1)	.11 Å	90°	90°	0°
	.11	0	120	90
	.14	90	30	90
Ba(2)	.10	90	90	0
	.11	0	120	90
	.11	90	30	90
V	.09	90	90	0
	.13	0	120	90
	.13	90	30	90
O(1)	.13	90	90	0
	.18	0	120	90
	.18	90	30	90
O(2)	.10	60	60	90
	.10	90	90	0
	.11	30	120	90

#### Discussion of the structure

ZACHARIASEN's structure for this family of crystals does not appear to have been adequately described. A clinographic projection of the atoms in the primitive rhombohedral cell is shown in Fig. 1. Unfortunately this view of the structure, which can be readily derived from the list of coordinates, does not give any impression of the actual environment of each atom. For this purpose a projection of the structure along the trigonal axis, as shown in Fig. 2, is preferable.

The interatomic distances are listed in Table 6, and the important bond angles are given in Table 7. The same information is shown graphically in Figs. 3 through 8.

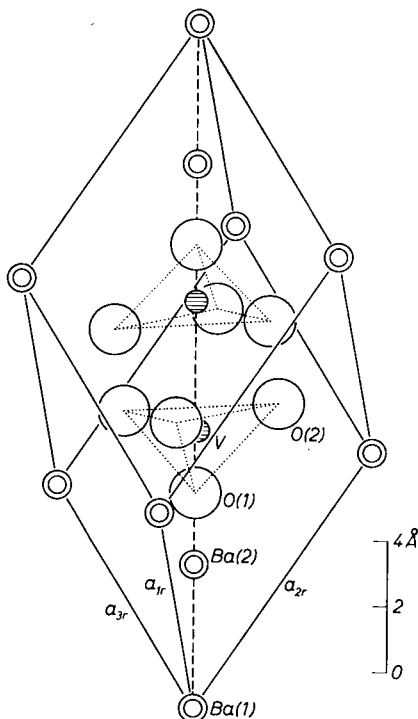
The vanadium and Ba(1) have simple and expected coordinations, but the Ba(2) and both kinds of oxygen atoms have unusual environments. The vanadium atom (Fig. 3) is coordinated to four oxygen atoms at the corners of an almost ideal tetrahedron, specifically one O(1) at 1.70 Å and three O(2) at 1.71 Å. The Ba(1) atom, which is located on an equipoint having  $\bar{3}$  symmetry (Fig. 4), has six O(2) neighbors at 2.76 Å, all equivalent by the  $\bar{3}$  symmetry and located at the corners of an octahedron elongated in the direction of the  $\bar{3}$  axis. The cause of this elongation is noted later.

Table 5. Observed and calculated structure factors

h k l	F <sub>o</sub> (hkl)	F <sub>c</sub> (hkl)	F <sub>o</sub> (hkl)	F <sub>c</sub> (hkl)	F <sub>o</sub> (hkl)	F <sub>c</sub> (hkl)	(F <sub>o</sub> /F <sub>c</sub> )	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub> (hkl)	F <sub>c</sub> (hkl)	F <sub>o</sub> (hkl)	F <sub>c</sub> (hkl)	F <sub>o</sub> (hkl)	F <sub>c</sub> (hkl)	(F <sub>o</sub> /F <sub>c</sub> )	F <sub>o</sub>	F <sub>c</sub>	
1 0 0	39.2	38.4	38.9	38.9	39.2	38.4	38.8	36.9		7 5 5	0.7	2.7	1.3	1.3	0.7	2.7	1.6	-1.7		
1 1 0	16.0	16.3	16.1	16.0	16.3	16.1	16.1	-13.7		7 6 1	35.1	35.9	35.3	34.9	35.8	35.3	35.4	34.3		
1 3 0	30.2	30.2	30.2	30.2	30.2	30.2	30.2	-19.4		2 6 8 9	68.6	68.6	68.6	68.3	68.9	67.4	68.4	68.3		
2 0 0	54.5	56.4	58.1	58.1	54.5	56.4	56.3	-55.9		3 3 2	4.5	4.0	3.7	5.1	4.3	4.1	4.3	4.1	-2.7	
2 1 0	0.6	0.6	0.6	0.6	0.6	0.6	3.9	1.1	-12.5	4 18 0	18.1	17.9	18.6	17.7	17.6	18.0	17.3	18.0	-17.3	
2 2 0	51.0	49.7	51.4	51.4	51.0	49.7	50.7	49.3		5 4 9	0.7	1.1	0.7	1.3	0.7	1.6	-0.9			
2 2 2	76.7	76.5	75.2	76.7	76.5	75.2	76.1	80.6		6 66.1	71.0	71.4	71.4	66.1	71.0	69.5	73.5	73.5		
3 0 0	3.6	2.7	3.5	3.5	3.6	2.7	3.3	-3.9		7 7 2	5.5	6.8	5.7	5.5	6.8	5.7	6.0	-4.8		
3 1 0	40.3	40.9	41.0	41.1	40.8	40.1	40.7	39.1		3 5 2	5.3	4.8	5.2	5.3	4.8	5.1	4.3	-4.3		
3 1 2	126.0	123.2	124.4	124.4	126.0	123.2	124.5	160.9		4 1 9	3.6	2.1	1.9	3.6	2.1	2.5	-0.3			
3 2 0	106.5	104.9	104.9	109.7	106.0	105.2	106.1*	123.7		5 54.0	52.6	55.9	54.0	52.6	55.9	54.2	55.2			
3 2 2	43.5	45.8	45.6	44.1	44.2	45.0	43.7	39.4		6 70.4	69.4	73.7	70.4	69.4	73.7	71.2	75.8			
3 3 0	31.9	32.0	32.2	31.9	32.9	32.2	32.3	29.8		7 0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.0			
3 3 2	41.6	41.7	41.3	41.6	41.7	41.3	41.5	-37.6		8 2 2	8.2	7.3	7.7	7.7	8.2	7.3	7.7	-9.4		
4 0 0	100.5	100.5	100.5	100.5	100.5	100.5	100.5	115.9		8 3 2	10.4	9.5	10.1	9.7	9.9	9.9	8.6			
4 1 0	92.6	92.9	92.9	95.1	94.3	91.6	93.2*	104.7		3 38.3	37.1	38.6	38.6	38.3	37.1	38.0	37.1			
4 2 0	7.1	8.3	7.9	9.2	7.0	7.7	7.9	7.5		8 4 2	37.7	37.6	38.5	37.7	37.8	37.0	37.7	36.9		
4 3 0	12.8	13.2	12.9	12.6	12.9	12.8	12.9	-12.8		3 68.1	68.0	69.0	68.9	68.1	65.8	68.0	68.6			
4 3 2	68.1	66.9	67.9	68.1	67.8	65.4	67.4	68.0		4 6.3	5.3	7.6	7.6	6.3	5.3	6.4	6.0			
4 4 0	117.5	115.3	116.3	116.3	117.5	115.3	115.7*	142.4		8 5 2	61.6	62.8	62.0	62.0	60.6	60.6	59.9	59.9		
5 0 0	79.7	73.9	73.1	74.8	70.2	72.6	74.4	70.1		3 4.2	5.6	4.8	0.2	3.4	4.5	3.7	-1.5			
5 1 0	19.6	19.5	20.1	19.7	19.9	19.1	19.6	19.5		4 16.7	16.9	17.3	16.9	16.8	16.3	16.8	-16.4			
5 1 2	25.5	25.0	26.1	26.1	25.5	25.0	25.5	-25.9		5 2.5	4.5	4.0	4.0	2.5	4.5	3.7	-3.0			
5 2 0	10.8	10.6	11.4	11.4	11.0	11.5	11.1	-11.3		8 6 2	6.5	7.0	6.8	6.9	6.3	6.6	-5.0			
5 2 2	19.3	18.7	19.2	19.2	19.6	18.6	19.1	-17.6		3 55.2	54.5	57.2	55.1	55.2	53.9	55.2	-15.3			
5 3 0	40.3	39.6	40.7	39.9	40.8	40.2	40.4	39.4		4 4 3	4.2	5.7	4.8	4.6	4.2	4.6	3.6			
5 3 2	17.2	17.9	17.8	17.2	17.4	17.3	17.5	-16.9		5 62.9	62.3	63.0	63.3	62.5	62.2	62.7	61.8			
5 4 0	88.9	89.7	88.2	88.9	89.0	88.0	88.8	95.8		8 7 3	2.9	3.3	5.5	6.9	4.5	3.2	3.7	-3.5		
5 4 2	10.9	7.8	7.7	7.8	10.5	8.0	8.8	6.8		4 56.4	56.3	56.7	56.7	56.7	56.7	56.7	57.2			
6 0 0	10.7	10.8	10.4	10.8	10.3	10.9	10.6	-9.6		5 10.3	9.9	10.4	10.3	9.9	10.4	10.2	-10.7			
6 2 0	42.0	40.4	41.8	42.3	41.8	40.7	41.5	-1.1		6 3.2	3.9	0.8	3.2	3.9	0.8	2.6	0.7			
6 3 0	78.4	74.6	78.9	78.9	78.4	74.6	77.3	82.2		7 2.6	1.3	2.3	2.6	1.3	2.3	2.1	1.7			
6 3 2	35.0	36.0	35.9	35.4	35.9	34.8	35.5	35.2		8 56.7	56.7	56.7	56.7	56.7	56.7	56.7	57.2			
6 4 0	62.9	64.8	64.0	63.6	64.6	63.5	63.9	62.3		9 4 3	4.4	5.2	5.2	5.4	5.9	5.9	5.3	-2.6		
6 4 2	4.6	4.8	3.6	3.5	4.6	5.4	4.4	4.3		4 12.6	12.0	12.5	12.5	12.6	12.0	12.4	-14.0			
7 0 0	11.1	11.2	11.0	11.0	11.2	11.1	11.1	9.7		5 59.2	58.4	59.2	60.0	59.7	57.8	59.0	57.4			
7 1 0	36.2	36.1	37.1	37.1	36.2	36.1	36.5	36.9		6 7.8	7.7	8.9	8.9	7.8	8.1	8.9	-8.9			
7 2 0	63.9	62.9	62.3	62.3	62.3	60.9	61.8	63.3		9 7 4	52.8	52.9	53.1	53.0	52.7	52.9	50.2			
7 3 0	58.6	59.7	59.8	58.8	59.5	58.5	59.1	-57.3		5 49.0	48.3	49.2	49.1	49.2	47.9	48.8	48.0			
7 4 0	3.4	2.8	2.2	4.4	1.2	2.7	2.8	3.7		5 59.2	58.4	59.2	60.0	59.7	57.8	59.0	57.4			
7 5 0	4.6	4.4	3.9	3.9	4.6	4.4	4.5	3.6		6 7.8	7.7	8.9	8.9	7.8	8.1	8.9	-8.9			
7 5 1	56.2	56.1	57.1	57.1	56.2	56.1	56.5	56.9		9 7 4	52.8	52.9	53.1	53.0	52.7	52.9	50.2			
7 5 2	6.1	4.1	4.4	4.4	6.1	4.1	4.9	4.9		6 9 3	9.1	8.8	8.5	9.0	9.2	9.0	-8.9			
7 5 3	58.6	59.7	59.8	58.8	59.5	58.5	59.1	-57.3		7 6.5	4.2	5.3	5.3	6.5	4.2	5.3	-5.3			
7 5 4	10.1	10.8	10.5	10.2	10.7	10.7	10.5	-11.6		9 8 4	7.7	9.3	8.4	8.9	8.4	8.6	8.5	-7.8		
7 5 5	51.4	51.1	51.9	51.7	51.3	49.3	51.1	51.3		5 9.9	9.2	9.4	9.1	9.4	10.1	9.5	-9.8			
7 5 6	4.2	1.9	2.9	2.1	3.1	3.9	3.0	1.2		6 3 4	4.4	5.2	5.2	5.4	5.9	5.9	5.3	-2.6		
7 5 7	46.3	47.1	47.1	46.7	46.8	46.0	46.7	46.4		7 64.1	60.5	60.6	63.4	63.1	61.7	62.2	63.8			
7 5 8	69.5	70.4	70.4	70.2	68.1	69.8	70.2	70.2		8 56.2	54.4	54.9	54.9	56.2	54.4	55.2	53.2			
7 5 9	3.6	5.2	5.3	4.5	4.2	5.4	4.7	-4.4		9 9 5	4.8	5.5	4.0	4.8	5.5	4.0	4.8	-4.3		

Table 5. (Continued)

h	k	l	$F_o(hkl)$	$F_o(klh)$	$F_o(hkh)$	$F_o(khl)$	$F_o(hlk)$	$F_o(klh)$	$F_o(lkh)$	$\langle F_o \rangle$	$F_c$	h	k	l	$F_o(hkl)$	$F_o(klh)$	$F_o(lkh)$	$F_o(khl)$	$F_o(hlk)$	$F_o(lkh)$	$\langle F_o \rangle$	$F_c$	
-2	-2	4	72.0	74.2	72.7	72.0	74.2	72.7	73.0	73.7	73.7	-4	-3	1	17.7	18.1	17.9	17.8	17.9	17.7	17.8	17.4	
-3	-1	1	16.7	16.9	16.7	17.0	17.0	16.7	16.8	-15.7	-15.7	2	66.8	67.3	67.5	66.8	67.5	66.7	67.1	66.7	67.1	66.3	
2	12.5	12.5	12.0	11.9	12.5	12.6	12.3	-12.0	12.3	-12.0	-12.0	3	18.4	19.1	18.6	18.5	18.7	18.6	18.6	18.6	19.0	19.0	
3	20.0	20.4	20.0	18.3	20.2	19.8	19.8	20.0	19.8	20.0	20.0	-4	-4	1	13.9	14.2	13.7	13.9	14.2	13.7	13.9	-14.1	4.5
4	62.1	62.5	62.9	57.9	63.6	61.9	61.8	59.5	61.8	59.5	59.5	2	4.5	4.9	5.3	4.5	4.9	5.3	4.9	5.3	4.9	4.5	
-3	-2	1	35.9	35.9	36.2	36.4	36.1	35.8	36.0	34.9	34.9	-5	-1	1	75.4	76.4	77.0	75.8	77.1	74.8	76.1	78.2	78.2
2	8.2	7.3	7.3	8.0	7.7	7.0	7.6	-7.5	7.6	-7.5	-7.5	2	20.3	20.2	20.7	19.9	20.5	20.0	20.3	19.7	19.7	19.7	
3	11.4	11.4	11.0	11.0	11.8	11.1	11.3	-12.0	11.3	-12.0	-12.0	-5	-2	1	15.9	15.8	15.5	15.5	16.0	15.7	15.7	15.4	
4	11.2	11.5	11.4	11.5	12.2	11.5	11.5	12.4	11.5	12.4	12.4	2	60.7	60.6	61.8	59.6	61.3	59.8	60.6	57.3	57.3	57.3	
-3	-3	1	97.9	94.9	94.9	97.9	94.9	94.9	95.9	105.5	105.5	-5	-3	1	20.2	20.2	20.4	20.1	20.8	20.4	20.3	-20.8	-20.8
2	26.6	26.7	26.7	26.6	26.7	26.7	26.7	25.2	26.7	25.2	25.2	2	11.3	11.4	11.7	11.8	11.7	11.9	11.6	12.9	12.9	12.9	
3	12.7	12.1	12.6	12.7	12.1	12.6	12.5	-12.5	12.5	-12.5	-12.5	-5	-4	1	13.1	12.6	12.6	12.6	12.6	12.6	12.7	-11.7	-11.7
-4	-1	1	31.9	32.3	32.5	32.0	32.1	31.3	32.0	31.1	31.1	-5	-5	1	37.8	37.6	37.8	37.8	37.6	37.8	37.7	36.9	36.9
2	8.9	9.9	9.1	9.1	9.2	8.5	9.1	-9.4	9.1	-9.4	-9.4	-6	-1	1	9.3	9.1	9.7	9.4	9.0	8.9	9.2	10.4	10.4
3	11.0	11.2	11.1	10.7	11.4	10.8	11.0	-11.4	12.1	11.9	12.0	-6	-2	1	12.1	11.9	12.0	11.8	12.0	11.6	11.9	-12.8	-12.8
-4	-2	1	84.0	82.6	85.0	85.5	85.0	83.6	84.3	90.2	90.2	-6	-3	1	10.7	10.4	10.4	10.6	10.6	11.6	10.7	-10.3	-10.3
2	35.7	36.6	37.2	35.9	36.7	36.0	36.3	36.2	36.3	36.2	36.2	-6	-4	1	29.2	29.6	29.8	28.6	29.3	29.5	29.3	28.0	28.0
3	11.1	11.1	11.2	10.8	10.7	10.5	10.9	-11.0	10.9	-11.0	-11.0												

Fig. 1. One unit cell of  $Ba_3(VO_4)_2$ 

The Ba(2) atom has a curious ten-fold coordination, illustrated in Fig. 5. The ten-fold coordination occurs in three shells having distances of 2.61, 2.80, and 2.94 Å. Only one oxygen atom, namely O(1), has the abnormally short distance of 2.61 Å. Three O(2) atoms, designated O(2d) in Fig. 5, are at the intermediate distance 2.80 Å. These atoms, and the O(1) atom first mentioned, form a distorted tetrahedron



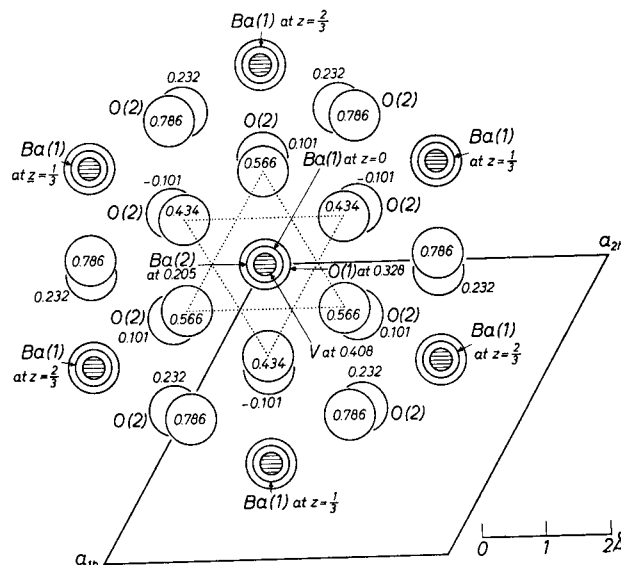


Fig. 2. Projection of the  $\text{Ba}_3(\text{VO}_4)_2$  structure along the trigonal axis. The numbers within the circles are the  $z$  parameters in the hexagonal triple cell

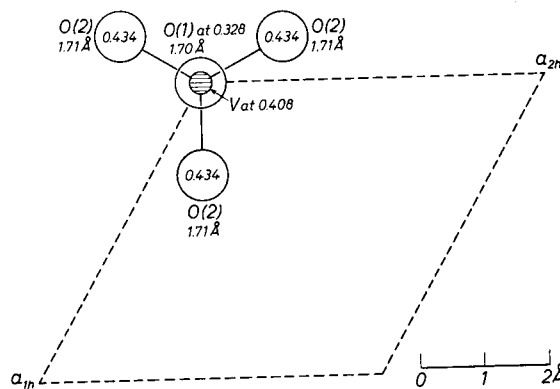


Fig. 3. Environment of the vanadium atom. For each atom is given its designation, its hexagonal  $z$  parameter and its distance from the central atom

about  $\text{Ba}(2)$ . The other six oxygen atoms at the extreme distance of 2.94 Å, are equivalent  $\text{O}(2)$  atoms on the same  $z$  level.

The three  $\text{O}(2)$  atoms, labelled  $\text{O}(2d)$  in Fig. 5 and Fig. 4, outline an equilateral-triangular face common to the coordination polyhedra of oxygen about  $\text{Ba}(2)$  and  $\text{Ba}(1)$ . Since  $\text{Ba}(1)$  is on a  $\bar{3}$  location, the

Table 6. *Interatomic distances*

Atoms	Distance	e. s. d.	Multiplicity	Illustrations
V—O(1)	1.70 Å	.03 Å	1	Fig. 3
V—O(2)	1.71	.03	3	
Ba(1)—O(2 <i>d</i> )	2.76	.01	6	Fig. 4
Ba(2)—O(2 <i>b</i> )	2.94	.02	3	Fig. 5
Ba(2)—O(2 <i>e</i> )	2.94	.02	3	
Ba(2)—O(2 <i>d</i> )	2.80	.02	3	
Ba(2)—O(1)	2.61	.02	1	
O(1)—V	1.71	.03	1	Fig. 6
O(1)—Ba(2)	2.61	.02	1	
O(1)—O(2)	2.78	.03	3	
O(2)—Ba(1 <i>a</i> )	2.76	.01	1	Fig. 7
O(2)—Ba(2 <i>a</i> )	2.80	.02	1	
O(2)—Ba(2 <i>b</i> )	2.94	.02	2	
O(2)—V	1.71	.03	1	
O(2)—O(2 <i>c</i> )	2.98	.03	2	
O(2)—O(2)	2.78	.03	2	
O(2)—O(2 <i>a</i> )	3.22	.03	2	
O(2)—O(1)	2.78	.03	1	
V—Ba(1 <i>a</i> )	3.68	.02	3	
V—Ba(2 <i>b</i> )	2.52	.02	3	
Ba(2 <i>b</i> )—Ba(2 <i>a</i> )	3.71	.01	3	
Ba(2 <i>b</i> )—Ba(1 <i>a</i> )	4.30	.01	6	
Ba(2 <i>a</i> )—V	4.34	.02	3	
Ba(2 <i>a</i> )—Ba(1 <i>a</i> )	4.37	.01	2	

Table 7. *Interatomic angles*

Atoms	Angle	e. s. d.	Multiplicity	Illustration
O(2)—V—O(2)	108.8°	.4°	3	Fig. 3
O(1)—V—O(2)	109.2	.3	1	
O(2 <i>d</i> )—Ba(1)—O(2 <i>d</i> )'	114.6	.2	6	Fig. 4
O(2 <i>e</i> )—Ba(2)—O(2 <i>b</i> )	60.9	.3	3	Fig. 5
O(2 <i>b</i> )—Ba(2)—O(2 <i>e</i> )'	56.4	.3	3	
O(2 <i>d</i> )—Ba(2)—O(2 <i>d</i> )	64.3	.3	3	
O(1)—Ba(2)—O(2 <i>e</i> )	78.4	.2	3	
O(1)—Ba(2)—O(2 <i>b</i> )	78.4	.2	3	
O(1)—Ba(2)—O(2 <i>d</i> )	142.0	.9	3	
Ba(2)—O(1)—V	180.0		1	Fig. 6
Ba(1 <i>a</i> )—O(2)—Ba(2 <i>a</i> )	103.5	.3	1	Fig. 7
Ba(1 <i>a</i> )—O(2)—V	109.9	.5	1	
Ba(2 <i>a</i> )—O(2)—V	146.6	.7	1	
Ba(2 <i>b</i> )—O(2)—Ba(2 <i>b</i> )	156.8	.7	1	
Ba(1 <i>a</i> )—O(2)—Ba(2 <i>b</i> )	97.9	.4	2	
Ba(2 <i>b</i> )—O(2)—V	94.7	.5	2	
Ba(2 <i>b</i> )—O(2)—Ba(2 <i>a</i> )	80.5	.4	2	

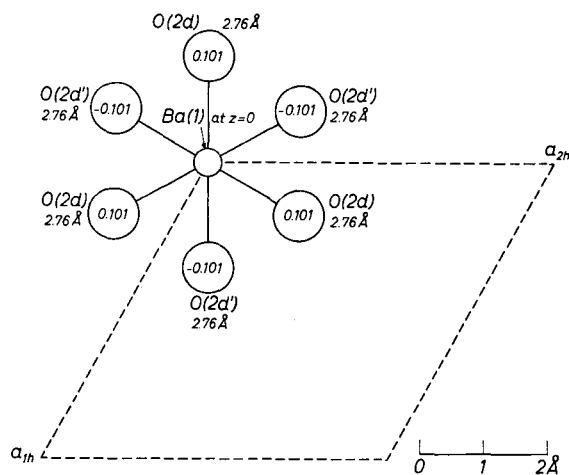


Fig. 4. Environment of Ba(1)

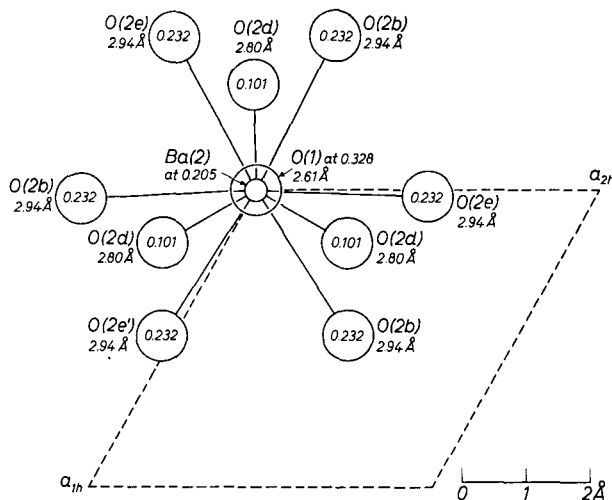


Fig. 5. Environment of Ba(2)

$\bar{3}$  axis of the structure is the locus of sets of three barium-coordination polyhedra connected together in a sequence: Ba(2)—Ba(1)—Ba(2). [A vanadium tetrahedron shares a vertex, namely O(1), with the ten-fold Ba(2) polyhedra on each end of this sequence]. The sharing of triangular faces common to pairs of coordination polyhedra is evidently related to the abnormal elongation of the octahedral coor-

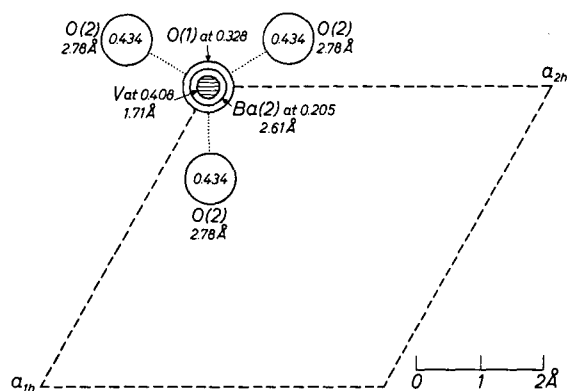


Fig. 6. Environment of O(1)

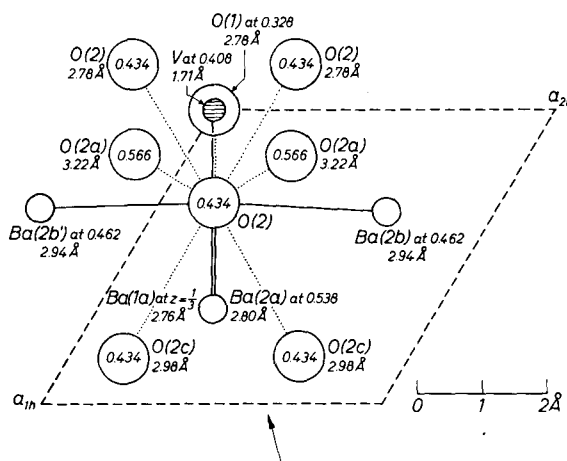


Fig. 7. Environment of O(2)

dination group about the middle Ba(1). This coordination suggests that there is a strong repulsion between pairs of neighboring barium atoms in the sequence, and this, in turn, suggests that both the Ba(1) and Ba(2) atoms are in an ionic state.

The environment of O(1), shown in Fig. 6, is relatively simple. Its only nearby metal neighbors are V and Ba(2), both on the same  $\bar{3}$  axis.

The environment of O(2), shown in Figs. 7 and 8, is a little more complicated. Its 5-fold metal coordination includes V at 1.71 Å, Ba(1a)

and Ba(2*a*) at about 2.78 Å, and 2 Ba(2*b*) at 2.94 Å. These comprise a distorted trigonal dipyramid about O(2).

### The electrostatic-valence balance

The curious coordinations of Ba(2) and O(2) invite an attempt to describe the bonding in terms of PAULING's electrostatic-valence rule<sup>5</sup>. The different distances from Ba(2) to its ten surrounding oxygen atoms presents a complication, but the regular V—O and Ba(1)—O distances permit assigning the bond strengths from V and Ba(1) with confidence. The items involved in bond-strength coordinations are listed in Table 8. In Table 8*b*, it is seen that the O(1) receives a strength of 5/4 from V, and since the only other bond is from Ba(2), this abnormally short bond must be assigned a strength of 3/4, in order to have the sum of the bonds to O(1) equal 2. This result can then

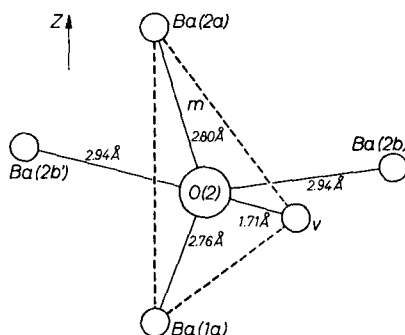


Fig. 8. Environment of O(2) viewed in the direction designated in Fig. 7 by an arrow

Table 8. *Electrostatic-valence bonds*

#### 8a. Bonds donated

Atom	Number of bonds	Acceptors	Distance	Strength	Total donated
V	4	O(1) + 3O(2)	1.7 Å	$\frac{5}{4} = \frac{1\frac{1}{2}}{1\frac{1}{2}}$	5
Ba(1)	6	6O(2)	2.76	$\frac{2}{6} = \frac{1}{3}$	2
Ba(2)	1	O(1)	2.61	$\frac{3}{4} = \frac{3}{4}$	} 2
		3O(2)	2.80	$\frac{1}{4} = \frac{1}{4}$	
		6O(2)	2.94	$\frac{1}{6} = \frac{1}{6}$	

<sup>5</sup> LINUS PAULING. The principles determining the structure of complex ionic crystals. *J. Amer. Chem. Soc.* **51** (1929) 1010–1026.

## 8b. Bonds received

Atom	Donor	Distance	Strength
O(1)	V	1.70 Å	$\frac{5}{4}$
	Ba(2)	2.61	assigned $\frac{3}{4}$
			$\Sigma: 2$
O(2)	V	1.71	$\frac{5}{4} = \frac{15}{12}$
	Ba(1a)	2.76	$\frac{2}{6} = \frac{4}{12}$
	Ba(2a)	2.80	$\frac{1}{4} = \frac{3}{12}$
	2 Ba(2b)	2.94	$2 \times \frac{1}{12} = \frac{2}{12}$
			$\Sigma: \frac{24}{12} = 2$

be entered for the Ba(2) derivation in Table 8a. If the three bonds of intermediate length from Ba(2) are each assigned a strength of 1/4, and if the six bonds of greatest length are each assigned a strength of 1/12, then both parts of Table 8 are seen to satisfy the electrostatic-valence rule.

Thermal motion of atoms on the  $\bar{3}$  axis

The angle V—O(1)—Ba(2) is 180°. The thermal ellipsoid of O(1) is oblate, implying that this atom makes excursions away from the three-fold axis to which it is formally assigned. In nepheline<sup>6</sup>,  $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ , one of the oxygen atoms in a sequence Si—O—Al is formally assigned to a three-fold axis also, but makes considerable excursions away from that axis. It appeared of interest, therefore, to see how large the excursion of O(1) in  $\text{Ca}_3(\text{VO}_4)_2$  might be. To investigate this, O(1) was assumed to have an isotropic temperature factor of 0.8 Å<sup>2</sup>, but was represented as 6 (or 3) equally placed fractional atoms in a circle about the  $\bar{3}$  axis. These approximations to an orbit lead to the same *R* value of 4.8% as the thermal ellipsoid of Table 4 for O(1), provided the radius of the orbit was about 0.18 Å. For this orbit radius, the deviation of the bond angle V—O(1)—Ba(2) from 180° is about 10°. We do not regard this result as having any important significance except to point out that the bond angle at O(1) must be within about 10° of a straight angle. Attempts to move either or both of the V or Ba(2) off the axis lead to larger *R* values.

This investigation was supported by grant number Ga-1308 from the National Science Foundation.

<sup>6</sup> THEODOR HAHN and M. J. BUEGER, The detailed structure of nepheline,  $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$ . Z. Kristallogr. 106 (1955) 308–338.