

The Crystal Structure of $\text{Ba}_3\text{V}_4\text{O}_{13}$

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$\text{Ba}_3\text{V}_4\text{O}_{13}$ crystallizes in the monoclinic system with unit-cell dimensions (from single-crystal data) $a = 16.100(3)$, $b = 8.947(3)$, $c = 10.173(3)$ Å, $\beta = 114.39(2)^\circ$, and space group $C2/c$, $z = 4$. The structure was solved using Patterson and Fourier techniques. The structure was refined by full-matrix least-squares methods, using 1604 ($I \geq 3\sigma(I)$) unique countermeasured reflections, to a conventional R of 0.028 (R_w 0.041). The structure comprises Ba^{2+} and $[\text{V}_4\text{O}_{13}]^{6-}$ ions. The $[\text{V}_4\text{O}_{13}]^{6-}$ polyanion consists of four corner-shared vanadium tetrahedra in a U-shaped arrangement for which the torsion angle between the vanadium atoms is $56.07(6)^\circ$. Other known $E_4\text{O}_{13}^-$ anions ($E = \text{Al, Si, P, or Cr}$) comprising corner-shared tetrahedra all have torsion angles that are $>172^\circ$. © 1987 Academic Press, Inc.

Introduction

In a study of the liquid–solid equilibria for the system V_2O_5 – BaO Kohlmuller and Perraud (1) reported the existence of three compounds, BaV_2O_6 , $\text{Ba}_2\text{V}_2\text{O}_7$ (two crystalline forms), and $\text{Ba}_3(\text{VO}_4)_2$. In a subsequent study (2) the compound $\text{Ba}_3\text{V}_4\text{O}_{13}$, and two reduced vanadates $\text{BaV}_{12}\text{O}_{30}$ and $\text{BaV}_8\text{O}_{21-x}$, were claimed to exist on the basis of X-ray diffraction (powder) and optical results. Recently the synthesis, unit-cell dimensions (refined using a least-squares technique, from powder data, $a = 16.087$, $b = 8.948$, $c = 10.159$ Å, $\beta = 114.52^\circ$) and the space group (Cc or $C2/c$) of $\text{Ba}_3\text{V}_4\text{O}_{13}$ were reported (3).

The crystal structures of three of the compounds in the BaO – V_2O_5 system have been determined. These are the 1:1

($\text{BaO}:\text{V}_2\text{O}_5$) compound BaV_2O_6 (4) that comprises infinite chains of corner-shared tetrahedra $[(\text{VO}_3)_n]^{n-}$; the 2:1 compound $\text{Ba}_2\text{V}_2\text{O}_7$ (5) in which two unique divanadate groups occur in sheets; and the 3:1 compound $\text{Ba}_3(\text{VO}_4)_2$ (6) in which discrete VO_4^{2-} tetrahedra exist. Concerning the apparent dimorphism of $\text{Ba}_2\text{V}_2\text{O}_7$ suggested by Kohlmuller and Perraud (1), Fotiev *et al.* (2) found the crystals studied by optical means to be monoclinic, whereas the structure reported for $\text{Ba}_2\text{V}_2\text{O}_7$ was for a triclinic crystal (5). As suggested in the report of the latter study, the possibility of dimorphism for $\text{Ba}_2\text{V}_2\text{O}_7$ should not be overlooked.

We report here the structure determination and refinement of $\text{Ba}_3\text{V}_4\text{O}_{13}$.

Experimental

A colorless prismatic crystal with developed faces 100 , $\bar{1}00$, 010 , $0\bar{1}0$, 001 , and

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00 $\bar{1}$ and of dimensions $0.05 \times 0.085 \times 0.185$ mm was selected from the preparation (3) and mounted on a silica capillary using Tyton 5 Minit adhesive. Crystal data were obtained using a Philips PW1100 computer-controlled four-circle diffractometer equipped with a graphite monochromator and using MoK α radiation. Lattice parameters and their standard deviations were obtained as the means of eight measurements made of the positions of 24 reflections $13^\circ < 2\theta < 38^\circ$ as orientation checks during the data collection.

Crystal data. Ba₃V₄O₁₃, $M = 823.8$, $a = 16.100(3)$, $b = 8.947(3)$, $c = 10.173(3)$ Å, $\beta = 114.39(2)^\circ$, $V = 1334.6$ Å³, D_m not measured as insufficient sample available, $D_c = 4.10$ g cm⁻³, $z = 4$, $F(000) = 1456$, $\mu = 113.4$ cm⁻¹ for MoK α (0.7107 Å) radiation. Space group Cc or $C2/c$ from systematic absences for hkl , $h + k = 2n + 1$ and for $h0l$, $l = 2n + 1$; $C2/c$ confirmed by successful refinement.

Intensity Measurements

Intensity measurements were made with the diffractometer and crystal described above. A unique data set was collected out to 2θ (MoK α) = 60° using the w - 2θ scan technique with a symmetric scan range of $\pm(1.2 + 0.3 \tan \theta)^\circ$ in 2θ from the calculated Bragg angle, at a scan rate of 0.04° sec⁻¹. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 1944 unique reflections measured 1604 were considered to be significantly above the background ($I \geq 3\sigma(I)$) and only these were used in the refinement. Three standard reflections, monitored at 3-hr intervals showed no significant variation in intensity. The data were processed in a manner described previously (7). An absorption correction was applied on the basis of the indexed crystal faces and dimensions (see above)—the maximum and minimum values of the transmission factors

were 0.5879 and 0.3912, respectively. No extinction correction was necessary. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were used (8). All calculations were carried out on the Monash University DEC VAX 11/780 computers; the major program used was SHELX (9).

Structure Solution and Refinement

The structure was solved for a general barium ion position using the Patterson method and the subsequent difference Fourier synthesis revealed the second barium position at $0, y, \frac{3}{4}$ on the twofold axis, thus indicating the centrosymmetric space group. Further difference Fourier syntheses enabled location of the two vanadium and seven oxygen positions—one of the latter also located on the twofold axis.

Full-matrix least-squares refinement with anisotropic thermal parameters for barium atoms and isotropic thermal parameters for vanadium and oxygen atoms resulted in convergence with $R = 0.028$ and $R_w = 0.041$. [$R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$ and $w = (\sigma^2(F))^{-1}$]. Forty-nine parameters were varied in the final cycles of refinement and at convergence the biggest shift to esd ratio was for U_{11} of O(5) and was -0.001 . The largest feature in the final difference Fourier synthesis was near V(1) and was $\sim 1.1 e$ Å³. Final parameters and their estimated standard deviations are given in Table I.²

² For a table of observed and calculated structure factors see NAPS document No. 04507 for 9 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 for up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$5. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

TABLE I
ATOMIC PARAMETERS FOR $Ba_3V_4O_{13}$
(ESD VALUES IN PARENTHESES)

Atom	x	y	z	U(iso) (\AA^2)
Ba(1)	0.2944(1)	0.6639(1)	0.3018(1)	<i>a</i>
Ba(2)	0.0	0.1186(1)	0.75	<i>a</i>
V(1)	0.0920(1)	0.1864(1)	0.5027(1)	0.010(1)
V(2)	0.1147(1)	0.5115(1)	0.3688(1)	0.011(1)
O(1)	0.1273(4)	0.3801(6)	0.5062(7)	0.027(1)
O(2)	0.1645(3)	0.6717(5)	0.4408(6)	0.018(1)
O(3)	0.1674(3)	0.4442(6)	0.2731(5)	0.019(1)
O(4)	0.1277(4)	0.0811(6)	0.4004(6)	0.024(1)
O(5)	-0.0202(4)	0.1669(6)	0.4537(6)	0.025(1)
O(6)	0.1455(3)	0.1336(5)	0.6771(5)	0.013(1)
O(7)	0.0	0.5630(9)	0.25	0.027(2)

^a Anisotropic thermal parameters are of the form

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	0.009(1)	0.011(1)	0.015(1)	0.000(1)	0.005(1)	0.002(1)
Ba(2)	0.012(1)	0.016(1)	0.013(1)	0.0	0.007(1)	0.0

Selected bond lengths and angles are given in Table II.

Discussion

The structure consists of Ba^{2+} cations and $[V_4O_{13}]^{6-}$ polyanions (Fig. 1). The polyanion is shown in Fig. 2 together with the numbering scheme used, and can be described as a twisted *U*-shaped arrangement of four corner-shared tetrahedra. The V-V distances in the polyanion range from 3.296(2) \AA for the closest corner-shared pair of tetrahedra to a maximum of 4.840(1) \AA for the V(2)-V(1) tetrahedra that have no oxygen atoms in common. The distance of each vanadium atom from planes defined by the three other vanadium atoms are given in Table II. The torsion angle V(1)-V(2)-V(2)-V(1) is 56.07(6) $^\circ$.

The vanadium to oxygen bond distances range from 1.646(6) to 1.820(6) \AA (mean 1.716 \AA). The average bridging V-O distance, 1.798 \AA , is greater than the average terminal V-O distance, 1.667 \AA ; a similar distribution of distances was observed for $Ba_2V_2O_7$ (5), where V-O bridged distances, mean 1.817 \AA , compared with terminal dis-

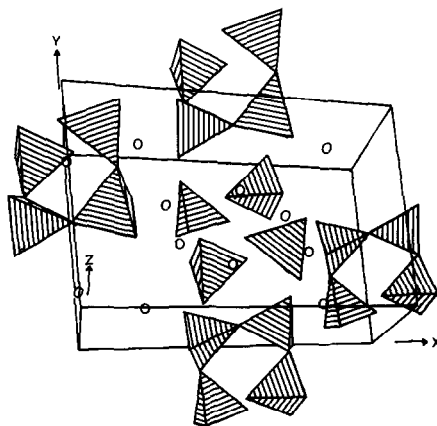


FIG. 1. A view of the structure of $Ba_3V_4O_{13}$ approximately perpendicular to the *xy* plane. Nowhere within the unit cell is a complete quartet of corner-shared tetrahedra. Open circles represent Ba in the unit cell.

tances with a mean of 1.686 \AA . For comparison with the V_2O_7 groups of divanadates (5) the tetravanadate ion here may be considered in two halves. Newman-type projections are provided of the oxygens around V(1) and V(2) looking along the V(1)-V(2) axis, and the V(2)-V(2) axis (Fig. 3) of the two "divanadate" halves. The oxygens around the V(1)-V(2) pair (V-O(br)-V 133.1(3) $^\circ$) are in an eclipsed conformation, while those around the V(2)-V(2) pair of tetrahedra (V-O(br)-V 150.3(3) $^\circ$) are in a more staggered arrangement. These observations agree with those

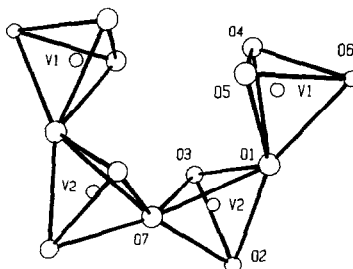


FIG. 2. Ortep diagram showing the linkage of vanadium tetrahedra in $Ba_3V_4O_{13}$.

of Hawthorne and Calvo (5) in that when the V–O(br)–V angle is less than 140° the divanadate groups are in the eclipsed conformation, whereas for V–O(br)–V > 140° the staggered conformation is observed. The torsion angles down V(1)–V(2) range from 8.4° in the case of O(4)–V(1)–V(2)–O(3) to 10.9° for O(5)–V(1)–V(2)–O(7); for the V(2)–V(2) pair these angles range from 16.0° for O(2)–V(2)–V(2)–O(2) to 21.7° for O(1)–V(2)–V(2)–O(3).

The thermal parameters of the bridging

TABLE II
SELECTED INTERATOMIC DISTANCES (Å) WITH
ESTIMATED STANDARD DEVIATIONS
IN PARENTHESES

Metal–Oxygen			
V(1)–O(4)	1.672(6)	V(2)–O(3)	1.646(6)
–O(5)	1.672(6)	–O(2)	1.658(5)
–O(6)	1.688(4)	–O(1)	1.773(7)
–O(1)	1.820(6)	–O(7)	1.800(2)
Metal–Metal			
V(1)–V(2)	3.296(2)	V(2)–V(2) ^a	3.480(2)
V(1)–V(1) ^a	4.757(2)	V(1)–V(2) ^a	4.840(1)
Barium contacts to oxygen out to 3.3 Å			
Ba(1)–O(5) ^b	2.736(6)	Ba(2)–O(4) ^g	2.676(5)
–O(3) ^c	2.763(5)	–O(4) ^h	2.676(5)
–O(3)	2.765(5)	–O(6)	2.738(6)
–O(6) ^d	2.810(4)	–O(6) ⁱ	2.738(6)
–O(2) ^e	2.833(5)	–O(7) ^j	2.849(9)
–O(6) ^f	2.851(4)	–O(5)	2.927(7)
–O(4) ^c	2.912(7)	–O(5) ⁱ	2.927(7)
–O(2)	2.971(7)	–O(2) ^j	3.171(5)
–O(1) ^f	3.123(5)	–O(2) ^k	3.171(5)
Selected bond angles			
O(4)–V(1)–O(5)	111.2(3)		
O(4)–V(1)–O(6)	109.8(2)		
O(4)–V(1)–O(1)	111.3(3)		
O(5)–V(1)–O(6)	107.7(3)		
O(5)–V(1)–O(1)	113.3(3)		
O(6)–V(1)–O(1)	103.1(2)		
O(3)–V(2)–O(2)	107.7(3)		
O(3)–V(2)–O(1)	107.8(3)		
O(3)–V(2)–O(7)	109.4(2)		
O(2)–V(2)–O(1)	110.3(3)		
O(2)–V(2)–O(7)	104.5(3)		
O(1)–V(2)–O(7)	116.8(3)		
V(1)–O(1)–V(2)	133.1(6)		
V(2)–O(7)–V(2)	150.3(3)		

TABLE II—Continued

Torsion angles (°) ^l			
1	2	3	4
O(3)–V(1)–V(2)–O(4)			–8.44(22)
O(7)–V(1)–V(2)–O(5)			–10.90(27)
O(2)–V(1)–V(2)–O(6)			–9.40(39)
O(3) ^a –V(2) ^a –V(2)–O(1)			–21.66(31)
O(2) ^a –V(2) ^a –V(2)–O(2)			–16.02(53)
V(1)–V(2)–V(2)–V(1)			56.07(6) ^o
Oxygen–oxygen around V(1)			
O(1)–O(4)	2.885(8)		
–O(5)	2.919(9)		
–O(6)	2.748(8)		
O(4)–O(5)	2.760(10)		
–O(6)	2.749(8)		
O(5)–O(6)	2.714(6)		
Oxygen–oxygen around V(2)			
O(1)–O(2)	2.817(8)		
–O(3)	2.763(10)		
–O(7)	3.043(7)		
O(2)–O(3)	2.669(8)		
–O(7)	2.736(5)		
O(3)–O(7)	2.815(7)		
Distances (Å) of atom from plane defined by three atoms			
Atom	Plane		
V(1) ^a	V(1)–V(2)–V(2) ^a		2.734(3)
V(2)	V(1) ^a –V(1)–V(2) ^a		2.112(2)

^a –x, y, 1/2 – z

^b 1/2 + x, 1/2 + y, z

^c 1/2 – x, 1/2 + y, 1/2 – z

^d –x, 1/2 – y, 1 – z

^e –x, 3/2 – y, 1 – z

^f x, 1 – y, z – 1/2

^g –x, –y, 1 – z

^h x, –y, 1/2 + z

ⁱ –x, +y, 3/2 – z

^j –x, 1 – y, 1 – z

^k x, 1 – y, 1/2 + z

^l Sign is positive if when looking from atom 2 to atom 3, in the list, a clockwise motion of atom 1 would superimpose it on atom 4.

oxygen atoms, O(1) and O(7) (mean 0.027 Å²) are larger than those of the terminal oxygen atoms (mean 0.020 Å²)—an unexpected result. It is suggested that since the terminal oxygen atoms are involved in co-

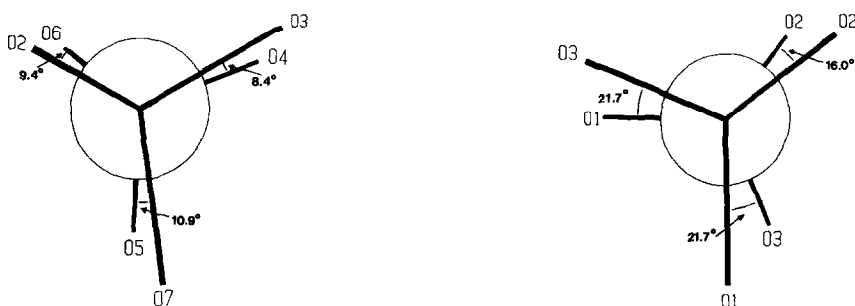


FIG. 3. Newman projections down (left) V(1)-V(2) and (right) V(2)-V(2) in $\text{Ba}_3\text{V}_4\text{O}_{13}$.

ordination to barium to a greater extent than the bridging oxygens, this results in smaller thermal vibrations.

On the basis of geometric and bond distance considerations, the coordination number of both barium ions has been taken to be nine. The geometry of Ba(1) is approximately that of a distorted tricapped trigonal prism with Ba-O distances ranging from 2.736(6) to 3.123(5) Å. Ba(2)-O distances range from 2.676(5) to 3.171(5) Å; however, the coordination polyhedron for this barium ion is not readily described in terms of the regular polyhedra. Individual diagrams (Fig. 4) are given for the barium ion polyhedra for which the mean Ba-O distance is 2.869 Å.

The valence bond strengths of Ba(1) and Ba(2)—see Table III—using the curve of

Brown and Wu (10), and based upon nine-coordination to oxygen, were 2.008 and 2.069, respectively, supporting the nine-coordination cutoff. Valence bond strengths for V(1) and V(2) for four-coordination were 5.110 and 5.046, respectively. Generally the bond strengths are in error by less than 5%. However, O(7) has an error of 8.9%, making it the largest.

The $E_4\text{O}_{13}^-$ ions known include those of Al^{III} , Si^{IV} , V^{V} , and Cr^{VI} . The torsion angle $E(1)-E(2)-E(3)-E(4)$ for Al^{III} in $\text{Na}_{14}\text{Al}_4\text{O}_{13}$ is 180° as there is a center of symmetry at the central bridging oxygen atom (11). The chain of four silicon-oxygen tetrahedra in $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ (12) appears to resemble that in the $\text{Al}_4\text{O}_{13}^{4-}$ ion above. However, it is not restricted by a center of symmetry and its torsion angle (Si-Si-Si-Si) is $177.4(2)^\circ$.

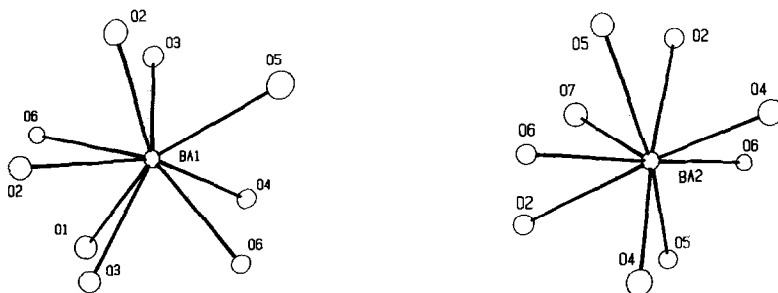


FIG. 4. The barium ion coordination spheres in $\text{Ba}_3\text{V}_4\text{O}_{13}$.

TABLE III
BOND STRENGTHS FOR Ba₃V₄O₁₃^a

	Ba(1)	Ba(2)	V(1)	V(2)	Σ
O(1)	0.116		0.921	1.053	2.090
O(2)	0.395 ^b	0.105 0.105 ^c		1.481	1.981
O(3)	0.548 ^b			1.538	2.086
O(4)	0.190	0.343 0.343 ^c	1.419		1.952
O(5)	0.294	0.183 0.183 ^c	1.418		1.895
O(6)	0.465 ^b	0.293 0.293 ^c	1.352		2.110
O(7)		0.222		0.975, 0.975 ^d	2.172
Σ	2.008	2.070	5.110	5.047	

^a Bond strengths in valence units from formulas of Brown and Wu (14).

^b Summed bond strength contributions for all Ba(1)-O(x).

^c Not included in individual oxygen bond strengths as they are from symmetry-related equivalent.

^d Not included in V(2) bond strengths as it is from symmetry-related equivalent vanadium.

In the compound reported here the V-V-V-V torsion angle is 56.07(6)°, quite atypical of this small group of compounds. In (NH₄)₂[Si(P₄O₁₃)] the torsion angle is 177.32(3)° (13), and finally, having taken the compounds in order of increasing oxidation state of "E," in Rb₂Cr₄O₁₃ (14) the Cr-Cr-Cr-Cr torsion angle is 172.30(5)°. Thus with the exception of Ba₃V₄O₁₃, reported here, all of the "E₄O₁₃" ions have M-M-M-M torsion angles that are >172°, all thus resembling four-tetrahedra chains rather than U-shaped ions as in Ba₃V₄O₁₃.

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