

X-RAY DIFFRACTION STUDY OF SODIUM AND POTASSIUM OXYGEN VANADIUM BRONZES $\text{Me}_{0.33}\text{V}_2\text{O}_5$

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An x-ray diffraction study of the structure of sodium and potassium vanadium bronzes $\text{Me}_{0.33}\text{V}_2\text{O}_5$ has been made. Positions of atoms in the structure recently determined by Wadsley have been refined by the use of sections of the electron density function. Crystallochemical similarity between the bronzes and the higher vanadium oxides has been established.

An investigation of vanadico-vanadates, or more correctly, vanadium bronzes [1], with a formula usually written $m \cdot \text{Me}_2\text{O} \cdot n\text{V}_2\text{O}_4 \cdot p\text{V}_2\text{O}_5$ (Me—an alkali metal, m, n, p —integers) or $\text{Me}_x\text{V}_2\text{O}_5$ ($0 < x < 1$) is interesting from both theoretical and practical points of view. A number of points were not clear in the crystal chemistry of these compounds, e.g., the valence of vanadium ions in the structure, the unusual properties of the vanadium bronzes, their high electrical conductivity, metallic luster, chemical inertness and others. Of practical interest is the clarification of the role of the bronzes in the vanadium catalysts and in the making of sulfuric acid. Entirely contradictory views exist in the literature on this problem. Canneri [2] believes that vanadium bronzes are the active components in vanadium catalysts. If vanadium exists in these compounds in an intermediate valence state and is therefore easily reduced or oxidized, then his opinion is reasonable. But an opposite view is held by G. K. Boreskov [3], who believes that formation of the vanadium bronzes causes thermal poisoning of the catalysts. Until now it had not been definitely established which of these views is correct.

The first step toward the solution of these problems is the determination of the structure of vanadium bronzes and to this the present paper is devoted.

Sodium and potassium vanadium bronzes were obtained during investigation of the contact process of preparation of sulfuric acid, i.e., of systems containing V_2O_5 and sodium and potassium sulfates and vanadates [4, 5, 6]. The bronzes form long, black, flat acicular crystals with bluish metallic luster. Their composition is $(\text{K}, \text{Na})_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ or $(\text{K}, \text{Na})_{0.33}\text{V}_2\text{O}_5$. The crystals have a fairly large number of faces. The simple forms are the pinacoids $\{102\}$, $\{101\}$, $\{100\}$ and $\{001\}$. The development of different faces varies from crystal to crystal.

Structural analysis by the Laue method shows that the crystals are monoclinic and belong to the Laue class $\text{C}_{2h}-2/m$. The dimensions of the unit cell were determined from photographs taken with an RKOP camera and then refined from photographs taken with the 114.56 mm RKU camera, and $\text{FeK}\alpha$ radiation. The reflections 900, 902 and 5010 were used with $\theta = 67-75^\circ$.

The following values were obtained for the lattice period of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ ($\lambda\text{FeK}\alpha = 1.93597 \text{ \AA}$):

$$\begin{aligned}
 a &= 10.039 \pm 0.003\text{\AA}, \\
 b &= 3.605 \pm 0.003\text{\AA}, \\
 c &= 15.335 \pm 0.003\text{\AA}, \\
 \beta &= 109^\circ 12' \pm 3' = 109.20^\circ
 \end{aligned}$$

The period b was determined from the 020 reflection on a powder photograph of the sodium vanadium bronze. The volume of the unit cell is therefore 524.2 \AA^3 .

Comparison of rotation photographs of sodium and potassium vanadium bronzes shows that their lattice periods are nearly identical. For this reason the above values were accepted for both vanadium bronzes.

The density of the potassium vanadium bronze was determined in a pycnometer as $\rho = 3.57 \text{ g/cm}^3$. For this density and the formula $\text{K}_2\text{V}_{12}\text{O}_{30}$, the number of molecules in the unit cell is $\sim 1(0.97)$. The value of density computed from the x-ray data is $\rho_{\text{roent}} = 3.60 \text{ g/cm}^3$.

The extinctions observed in the photographs indicate x-ray group No. 6 [7]. This group contains three space groups: $A 2/m$, $A/2$ and A_m . The choice of the correct space group was made by analyzing the dimensions of the unit cell and the symmetry of the oxides of vanadium, molybdenum, tungsten and of the tungsten bronzes. The structures of many of these oxides [8] and also of some of the alkali compounds of these metals [9] consist of layers of polyhedra one polyhedron in thickness. Most frequently the polyhedra are octahedra, sometimes trigonal dipyramids. In all cases the period corresponding to the height of the polyhedron ranges from 3.56 A to 4.10 A. With decrease in symmetry of the lattice, these periods increase; for the $2/m$ class they are 3.5-3.7 A, for $2_1/c$ - 4.0 to 4.1 A. In the vanadium bronzes this period is 3.60 A and they belong therefore to the highest symmetry class - $A 2/m$. This indicates also that in the bronze structure, all atoms lie in the mirror plane that is, their y coordinate is either 0 or $\frac{1}{2}$ (position 4 (i)), a fact confirmed by the absence of extra-structural reflections even in the much overexposed photographs.

That this choice of the space group is correct is confirmed by comparing reciprocal lattice photographs for alternating values of n : those for n equal to 0 or 2 are identical to those for n equal to 1 or 3, and this shows that they belong to the centrosymmetrical group - $A 2/m$.

The magnitude of the period b suggests also that the structure of the bronzes consists of octahedra or trigonal dipyramids; the compounds built of other polyhedra (tetrahedrons VO_4) have no periods comparable to 3.60 A [10, 11, 12].

The values of experimental structural amplitudes were determined from optical diffraction patterns. The total number of measured reflections was about 800 ($\text{MoK}\alpha$ -radiation), which includes practically the entire region of reflections. The intensity of reflections was estimated by comparison with a standard intensity scale [13]. To determine F as exactly as possible photographs with different exposures were used. Only the usual intensity factors were considered (absorption was disregarded).

The first information about structure was obtained from the Patterson projection $P(u, w)$ along [010]. The positions of the vanadium atoms in the unit cell were determined from the projection on the basis of published data on the structure of vanadium, molybdenum and tungsten oxides [8]. Wadsley's paper [14] with structural studies of the compound $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ (this is his formula for sodium vanadium bronze) appeared at this stage of our investigation. Wadsley determined the initial position of the vanadium atoms from an analysis of the interatomic vectors by the method of "superposition of images" [15]. The structure was determined by him from the projection of electron density along [010] by the use of about 250 nonzero structure amplitudes of $h0l$ type.

The coordinates of atoms given by Wadsley are listed in Table 1, while Fig. 1, A, shows the structure proposed by him.

To check Wadsley's results we constructed, using his coordinates, analogous projections for both sodium and potassium vanadium bronzes. All projections are very similar.

When the structure of the vanadium bronze is projected along axis Y, three oxygen atoms are covered by vanadium atoms and this makes it difficult to determine their positions. Wadsley avoided this difficulty by making two projections of the function of electron density; the projection for determining the position of vanadium atoms was based on distant reflections ($2 \sin \theta / \lambda > 0.8$), while the position of the oxygen atoms was determined by the use of differential synthesis. However, a more exact determination of the structure can be obtained not by the method of projections but from sections of the function $\rho(xyz)$. This was one of the reasons why we continued our study of this structure although Wadsley had already published his results.

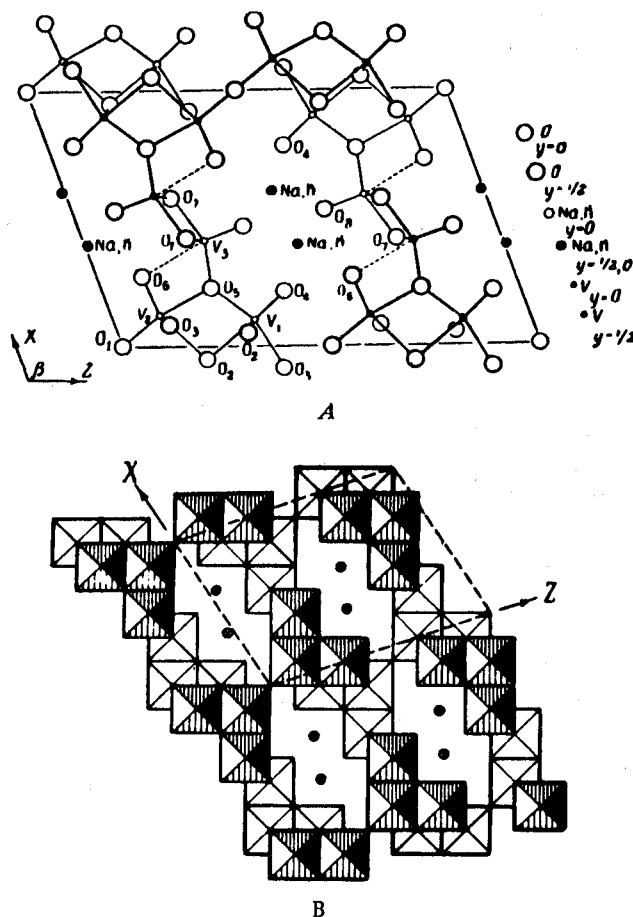


Fig. 1. Structure of sodium and potassium vanadium bronzes. A) Location of atoms in the structure; B) arrangement of polyhedra (⊗ - location of alkali atoms).

Another reason was that in the unit cell of the bronze, alkali atoms occupy only two of four available positions and this brings up the question of the distribution of the atoms and the "holes" in the structure. It was desired also to determine exactly the position of atoms in the potassium bronze, which was not studied by Wadsley.

These three circumstances made further investigations worthwhile in our opinion.

The section $\rho(x0z)$ was constructed by the use of 800 reflections, it is shown in Fig. 2. Two new approaches were used in the construction of this section. First, in our case (for group $A2/m$ all atoms lie in the mirror plane) the following relations hold almost exactly:

$$F(h0l) \cong M_2 F(h2l) \cong M_4 F(h4l) = \dots$$

$$F(h1l) \cong M_3 F(h3l) \cong M_5 F(h5l) = \dots$$

For this reason, to construct this section it is necessary only to use the amplitudes with $k = 0$ and 1. To diminish error in determination of reflection intensities we added also the amplitudes with $k = 2$ and 3. Second, at present Booth's method is used in determining the positions of maxima in two-dimensional synthesis. With large unit cells and division of sides into 48 parts (in summation) this method becomes rather crude. We avoided this difficulty by using another method.

TABLE 1

Coordinates of Atoms in the Sodium and Potassium Oxygen Vanadium Bronzes

Atoms	$K_{0.33}V_2O_5$ (our results from $\rho(x0z)$ section)	$Na_{0.33}V_2O_5$ (Wadsley's data)	ATOMS	$K_{0.33}V_2O_5$ (our results from $\rho(x0z)$ section)	$Na_{0.33}V_2O_5$ (Wadsley's data)
V_1	$x = 0.103$	0.103	O_4	0.222	0.219
V_2	$z = 0.337$	0.339	O_5	0.438	0.436
V_3	0.119	0.119	O_6	0.224	0.225
	0.117	0.117		0.265	0.264
	0.411	0.411	O_7	0.269	0.271
	0.289	0.289		0.107	0.108
K (Na)	0.414	0.394	O_8	0.421	0.419
	0.995	0.007		0.754	0.750
O_2	0.049	0.053		0.464	0.467
	0.813	0.811		0.396	0.396
O_3	0.079	0.078			
	0.637	0.633			

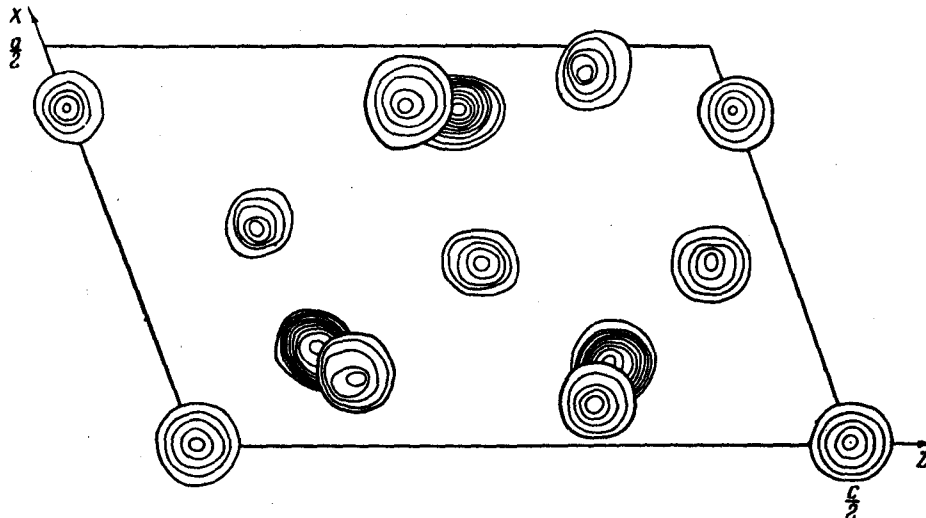


Fig. 2. Two-dimensional section of the function of electron density $\rho(x0z)$ for $K_{0.33}V_2O_5$.

The coordinates of the atoms in potassium vanadium bronze determined by us and the $\rho(x0z)$ sections are given in Table 1. Table 2 gives the corresponding interatomic distances.

Table 1 shows that our atomic coordinates agree well in almost all cases with those obtained by Wadsley.* We compare the positions of atoms in the structures of analogous sodium and potassium compounds on the assumption that the positions of vanadium and oxygen atoms are practically identical in these compounds.

TABLE 2

Interatomic Distances (in Å) in Potassium Vanadium Bronze

V ₁ -O ₄	1.61	V ₂ -O ₆	1.56	V ₃ -O ₈	1.55
V ₁ -O ₂	1.90	V ₂ -O ₃	1.89	V ₃ -O ₇	1.89
V ₁ -O ₂	2.30	V ₂ -O ₁	1.80	V ₃ -O ₇	2.00
V ₁ -O ₅	1.89	V ₂ -O ₆	2.16	V ₃ -O ₅	1.79
V ₁ -O ₃	1.99	V ₂ -O ₂	2.28	V ₃ -O ₆	2.68
O ₂ -O ₂	2.58	O ₃ -O ₂	2.55	O ₇ -O ₇	2.43
O ₂ -O ₅	2.65	O ₅ -O ₆	2.60	O ₆ -O ₆	2.60
O ₂ -O ₆	2.78	O ₂ -O ₅	2.60	O ₅ -O ₈	2.60
O ₄ -O ₅	2.65	O ₁ -O ₃	2.67	O ₅ -O ₇	2.69
O ₂ -O ₃	2.71	O ₃ -O ₅	2.71	O ₇ -O ₈	2.76
O ₂ -O ₅	2.81	O ₃ -O ₆	2.77	O ₇ -O ₈	2.87
O ₂ -O ₄	2.76	O ₁ -O ₆	2.66	O ₆ -O ₇	2.86
O ₃ -O ₄	2.85	O ₁ -O ₂	3.07	O ₆ -O ₇	3.14

TABLE 3

Distance	K _{0.33} V ₂ O ₅ ρ(xOz) section	Na _{0.33} V ₂ O ₅ (Wadsley's data)
Me-O ₈	2.50	2.46
Me-O ₈	2.49	2.75
Me-O ₄	2.56	2.51
Me-O ₆	2.57	2.29
Mo-Mo	1.68	2.22
O ₄ -O ₈	2.73	
O ₄ -O ₆	3.06	
O ₆ -O ₈	3.23	
O ₈ -O ₄	3.35	
O ₈ -O ₈	3.03	

Note: Me = an alkali metal.

It should be noted that the largest discrepancies occur in the case of those oxygen atoms which in the projection are covered by the atoms of vanadium. Our data are substantially different for the coordinates of the alkali atoms. In the structure these atoms are surrounded by seven oxygen atoms. The interatomic distances Me-O, according to Wadsley, range from 2.29 to 2.75 Å. In the structure of the potassium bronze, according to our data, these distances are almost equal—2.49, 2.50, 2.56, 2.57 Å. That the distances Me-O (within 0.06 Å) obtained by us from three-dimensional sections are equal is more probable than that they differ by as much as 0.46 Å and so our results appear to be more correct. The discrepancy in the position of the alkali atoms might be explained by the fact that

Wadsley determined positions of sodium atoms in the sodium bronze while our results are for the analogous potassium compound. However, our coordinates for Na obtained from the projection of ρ(xOz) for the sodium bronze also differ from his results.

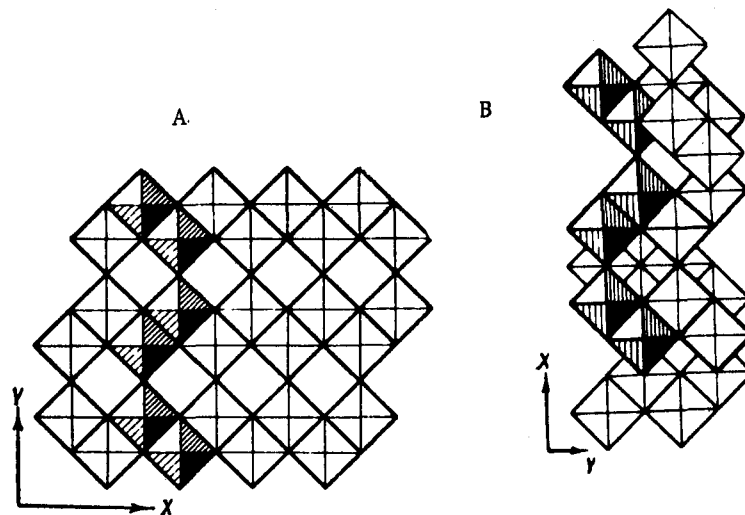


Fig. 3. Comparison of structures of vanadium pentoxide and vanadium bronze. A) grouping of polyhedra in V₂O₅; B) the grouping of polyhedra in Me_{0.33}V₂O₅.

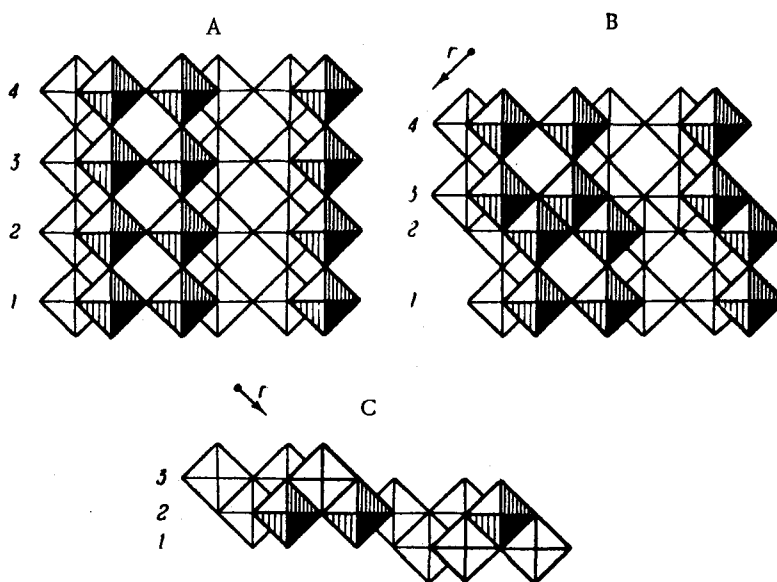


Fig. 4. The grouping of polyhedra in the structures. A) V_2O_5 ; B) $V_{12}O_{16}$ and C) $Me_{0.33}V_2O_5$.

The distance between two alkali atoms in $Na_{0.33}V_2O_5$ connected with each other by an axis of two-fold symmetry is 2.22 Å according to Wadsley, but according to our data it is 2.02 Å. The corresponding value for $K_{0.33}V_2O_5$ is 1.68 Å.

Noteworthy are the shortened (as compared with the normal 1.7–1.8 Å) distance V_1-O_4 (1.61 Å), V_2-O_6 (1.56 Å) and V_3-O_3 (1.55 Å). In general this shortening is observed in some vanadium, molybdenum and other transition elements [17]; in our case, however, the shortening is always in the direction vanadium–oxygen–alkali metal.

As can be seen from Fig. 1, the structure of vanadium bronze consists of strongly deformed octahedra VO_6 . This deformation is so great that some polyhedra, and especially those containing the V_3 atoms, could be considered trigonal dipyramids rather than octahedra; the distances $V-O$ in these polyhedra differ considerably from each other; they are 1.55, 1.79, 1.89, 2.00 and 2.68 Å. If the structure is idealized, that is, if it is considered as consisting of octahedra, then the grouping of the polyhedra can be rather easily visualized (Fig. 3, B). In this case the structure of bronze can be imagined as consisting of complex layers of octahedra infinitely extended in the directions \underline{x} and \underline{y} . The layers share the vertices of the octahedra and extensive empty spaces are present between them. These empty spaces or channels extend through the entire crystal in the direction of the Y axis. The alkali atoms lie in the channels.

The resemblance between the position of the octahedra in the structures of vanadium bronzes and in the higher vanadium oxides is easily seen. If the structure of a bronze is viewed in the direction normal to the xy plane, the layers will appear as zig-zag chains of octahedra analogous to those in V_2O_5 [18]; to see this, compare the shaded octahedra in Fig. 3. It is known that in the V_2O_5 structure the chains shown in Fig. 3 are in contact only at the vertices of the octahedra (Fig. 4, A). The structure of $V_{12}O_{26}$ [19] is obtained from that of V_2O_5 by connecting each third layer with the preceding one not by vertices but by the edges of the octahedra (Fig. 4, B; \underline{r} – displacement vector). If all layers are connected by octahedral edges, then a structure similar to that of $Me_2V_{12}O_{30}$ (Fig. 4, C) is obtained. There is, however, a significant difference; in the vanadium oxides the chains of octahedra have an infinite extent, while in the bronzes their length is limited to six octahedra.

All this is so if the structure is considered as consisting of ideal octahedra. But even if the actual polyhedra are considered the structures of the bronzes and the vanadium pentoxide have much in common.

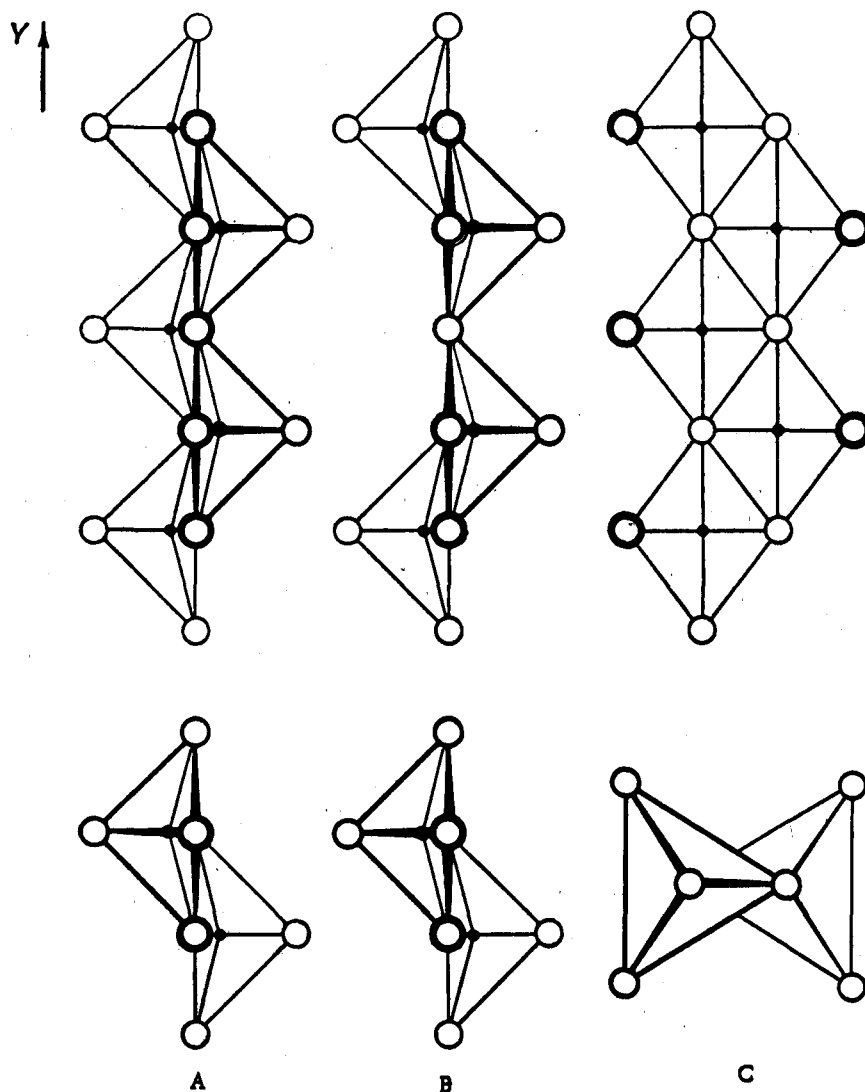


Fig. 5. Chains of trigonal dipyramids in the structure. A) V_2O_5 ; B) $Me_{0.33}V_2O_5$ and C) $KVO_3 \cdot H_2O$.

In V_2O_5 , vanadium atoms are surrounded by five oxygen atoms and form a trigonal dipyramid. But this dipyramid is peculiar because its four vertices (four oxygen atoms) all lie in almost the same plane. Attached by their edges the dipyramids form special chains shown schematically in Fig. 5. In the bronzes similar chains of dipyramids stretch along the y axis joining the layers of octahedra (Figs. 1, A and 5, B). In the structure of another vanadium compound, the potassium metavanadate monohydrate $KVO_3 \cdot H_2O$ [9], vanadium atoms are also surrounded by five oxygen atoms and the polyhedra join each other in approximately the same way (Fig. 5, B) but the chains are different from those of V_2O_5 or the bronzes.

The alkali atoms, as has already been mentioned, lie in the channels between the layers of the octahedrons VO_6 . Each alkali atom is surrounded by seven oxygen atoms and this group forms a polyhedron which is a combination of a trigonal prism and half an octahedron. The seven-fold coordination is rather rare but several occurrences of it are well known at present; the ion $(NaF_7)^{3-}$ has such a structure [20], and similar polyhedra are found in the structure of the intermetallic bismuth compound Bi_3Ni [20], etc.

This investigation of the structure of sodium and potassium vanadium bronzes $Me_{0.33}V_2O_5$ is the first step toward a crystallochemical study of these compounds.

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