THE CRYSTAL STRUCTURE OF METAROSSITE

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ABSTRACT

The crystal structure of metarossite, $Ca(VO_3)_2.2H_2O$, has been determined from three-dimensional Patterson and Fourier syntheses and has been refined by two-dimensional Fourier and difference methods. Vanadium co-ordination polyhedra, in the form of distorted trigonal bipyramids, share edges to form double chains parallel to [010]. These chains are linked through edges and corners to calcium co-ordination polyhedra, in the form of distorted square antiprisms, which share edges to form chains parallel to [100]. Long hydrogen bonds from the water molecules serve as additional links between the calcium and vanadium polyhedra.

INTRODUCTION

Metarossite is a hydrated calcium vanadate with the composition $CaO.V_2O_5.2H_2O$. It is soft and friable, yellow in colour, and forms as the dehydration product of rossite, $CaO.V_2O_5.4H_2O$. It is soluble in hot water but rossite crystallizes from the aqueous solution. Both minerals were first described by Foshag & Hess (1927) from specimens found in veinlets cutting carnotite-bearing sandstone in Bull Pen Canyon, San Miguel County, Colorado.

Metarossite is triclinic, space group $P\bar{1}$, with $a = 6.21_5 \pm 0.005$ Å, $b = 7.06_5 \pm 0.005$ Å, $c = 7.76_9 \pm 0.005$ Å, $\alpha = 92°58' \pm 10'$, $\beta = 96°39' \pm 10'$, $\gamma = 105°47' \pm 10'$, and two formula units per unit cell (Barnes & Qurashi, 1952). These data were obtained with a crystal selected from a specimen (Harvard No. 90650) from near Thompson's, Utah. The same crystal was used for the collection of intensity data in the present investigation of the structure of metarossite. It was tabular on $\{10\bar{1}\}$, had a rhomboidal cross-section with edges of 0.13 mm., and a thickness of 0.07 mm. Zero-level [010] Weissenberg photographs confirmed the presence of a small twin component (cf. Barnes & Qurashi, 1952, p. 416) with $\{10\bar{1}\}$ as the twin-plane.

EXPERIMENTAL

The $hk0$ and $0kl$ reflections were recorded on precession photographs ($\bar{\mu} = 30°$) with Mo K_α radiation ($\lambda = 0.7107$ Å) and multiple exposures. The $h0l$ reflections were recorded on zero-level Weissenberg photographs

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using multiple film techniques. Very few reflections with $(\sin \theta)/\lambda > 0.6$ were observed despite exposures of more than 100 hours.

Data for the calculation of a three-dimensional Patterson function were collected with equi-inclination [010] Weissenberg photographs using multiple film techniques. Because a high degree of accuracy was not required at this stage, and exposure times with Mo K_α radiation would have been very long, Cu K_α radiation ($\lambda = 1.5418$ Å) was employed except for the $h5l$ and $h6l$ reflections which were recorded with Mo K_α radiation. Thus all reflections for which $(\sin \theta)/\lambda < 0.5$ were obtained by a single setting of the crystal with the y-axis as oscillation axis.

All intensities were estimated visually and the usual Lorenz and polarization factors were applied. The three-dimensional data were not corrected for absorption. The calculated absorption coefficients for Mo K_α and Cu K_α radiations are 38.4 cm^{-1} and 330 cm^{-1}, respectively, and approximate corrections were made to the data for the three axial zones in the case of a few reflections (100, 010, 001, 1$\bar{1}$0, 10$\bar{1}$) which could only be recorded with Cu K_α radiation.

STRUCTURE ANALYSIS

An intensity distribution curve (Howells, Phillips & Rogers, 1950) was plotted for each of the three axial zones. The results pointed strongly to the centrosymmetrical symmetry of the space group $P\bar{1}$.

If the space group were $P1$ there should be 15 localized regions of high, and approximately equal, vector density in the asymmetric volume of Patterson space arising from interactions among the two calcium and four vanadium atoms. If the space group is $P\bar{1}$, however, 12 of these would overlap in pairs because of the centre of symmetry in the crystal structure; the remaining three (corresponding to Ca-Ca', V_1-V_1', V_2-V_2' vectors through the centre of symmetry) would be relatively of much lesser weight. All attempts to interpret axial projections of the Patterson function were unsuccessful, but a three-dimensional sharpened Patterson synthesis revealed six prominent concentrations of high, and approximately equal, vector density in the asymmetric volume, showing that the structure must have either a centre of symmetry or a close approximation to one. Reasonable co-ordinates for the Ca and V atoms were deduced from these data and were used to predict the location of the smaller vector density concentrations in the Patterson function corresponding to the Ca-Ca', V_1-V_1', V_2-V_2' vectors. The approximate atomic co-ordinates were confirmed by the presence of vector density concentrations of the expected magnitude (about one-half that of the regions of maximum density) at the predicted sites in the Patterson space.

The locations of five of the eight oxygen atoms in the asymmetric unit were then found by the application of superposition methods (Beevers & Robertson, 1950). The sites of the three remaining oxygen atoms were revealed by a three-dimensional Fourier synthesis for which the signs were obtained from structure factor calculations based on the atomic positions so far established.

Refinement of the Structure

The atomic co-ordinates were refined by two-dimensional Fourier and difference syntheses (Cochran, 1951). Difficulties due to overlapping of the electron-density peaks in the three axial projections were largely overcome by simultaneous refinement of the three zones.

TABLE 1. FRACTIONAL CO-ORDINATES OF THE
ATOMS. (All atoms in equipoints x,
y, z and $\bar{x}$, $\bar{y}$, $\bar{z}$.)

Atom	x	y	z
Ca	0.7595	0.4665	0.1470
V_1	0.4485	0.1020	0.3360
V_2	0.3750	0.5830	0.3450
O_1	0.3915	0.8400	0.4170
O_2	0.5170	0.3920	0.3835
O_3	0.8610	0.7555	0.3655
O_4	0.1050	0.4730	0.3345
O_5	0.1930	0.0635	0.2350
O_6	0.6245	0.1170	0.1870
O_7	0.4300	0.6000	0.1460
O_8	0.0070	0.7210	0.0130

Of the number of possible reflections, 74% of the $0kl$ reflections, 68% of the $h0l$ reflections, and 64% of the $hk0$ reflections were observed. Unobserved reflections were included in calculations of the R factor only for those planes for which the calculated structure factors were greater than the minimum observable values, F_m; in these cases F_o was assumed to be equal to $(\sqrt{2}/2)F_m$. The first structure factor calculations, for reflections with $(\sin \theta)/\lambda < 0.55$, gave R factors of 0.34, 0.15, and 0.40 for the $0kl$, $h0l$, and $hk0$ reflections, respectively, indicating that the y-co-ordinates were most in error. Refinement of the structure was carried out until these values had been reduced in each case to 0.11_5.

The best agreement between observed and calculated structure factors was obtained with the scattering-factor curves of Tomiie & Stam (1958) for Ca^{2+}, of Qurashi (1954) for V, and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for O. The final values adopted for the temperature-factor constant B, were 3.0 for Ca and V, and 4.0 for O.

The final values of the atomic co-ordinates are given in Table 1, and the observed structure amplitudes and calculated structure factors for the three principal zones are listed in Table 2. The final electron-density maps are reproduced in Figs. 1, 2, and 3.
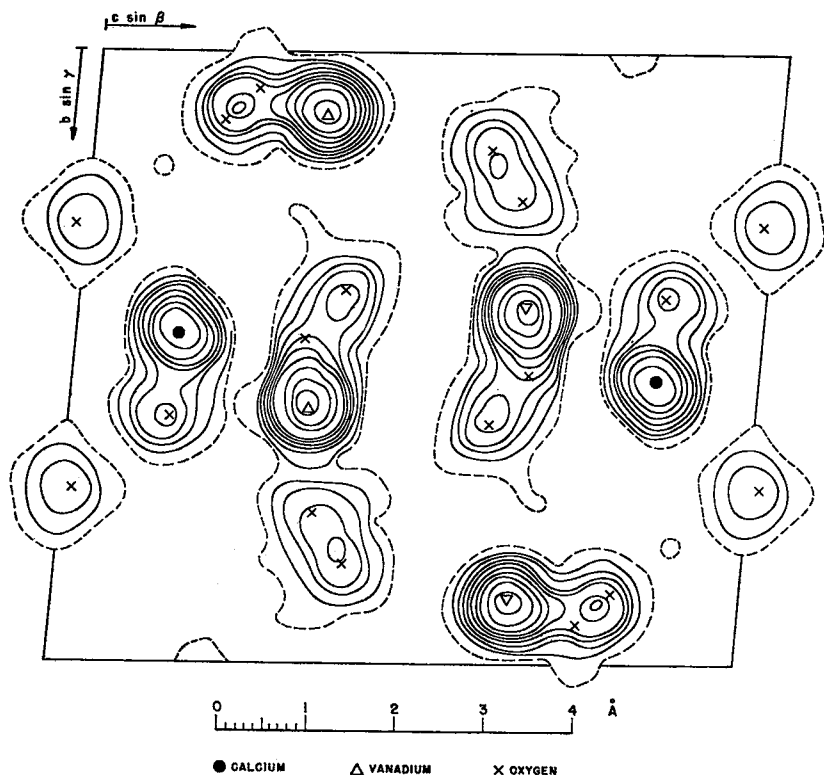

FIG. 1. Final electron-density projection along [100]. Contours at intervals of $2e.Å^{-2}$ from $8e.Å^{-2}$ (broken line) to $20e.Å^{-2}$, and at intervals of $5e.Å^{-2}$ above $20e.Å^{-2}$.

ACCURACY

Although the method of Cruickshank (1949) for the calculation of standard deviations does not strictly apply to the present data, because of the overlap in each of the three axial projections, it can be employed to obtain a rough estimate of the accuracy. On this basis the estimated standard deviations of the atomic parameters are 0.008 Å for Ca, 0.007 Å for V, and 0.026 Å for O; the e.s.d.'s of the interatomic distances are 0.027 Å for Ca-O, 0.027 Å for V-O, and 0.037 Å for O-O, and the e.s.d. for the angles O-V-O is 2°.

TABLE 2. STRUCTURE FACTOR DATA ($\frac{1}{2}$ absolute scale).

hkl	$|F_o|$	F_c	hkl	$|F_o|$	F_c	hkl	$|F_o|$	F_c
010	21.3	−22.0	043	6.7	− 6.4	027	8.2	− 6.8
020	23.6	+25.9	05$\bar{3}$	< 2.9	+ 0.4	037	3.1	− 2.9
030	16.9	−18.2	063	8.4	− 7.5	047	< 3.0	+ 2.6
040	11.3	− 9.8	07$\bar{3}$	< 3.0	+ 1.3	0$\bar{5}$8	7.2	+ 4.4
050	3.8	− 4.9	07$\bar{4}$	3.1	− 3.4	04$\bar{8}$	4.4	− 3.6
060	12.5	−11.3	06$\bar{4}$	3.8	+ 4.2	03$\bar{8}$	3.1	+ 2.1
070	3.1	+ 2.9	05$\bar{4}$	8.1	− 7.3	02$\bar{8}$	7.3	− 7.8
080	< 3.1	+ 0.3	04$\bar{4}$	13.6	+10.8	0$\bar{1}$8	4.8	− 4.6
0$\bar{8}$1	9.4	− 7.6	03$\bar{4}$	6.6	+ 9.0	008	< 3.1	+ 1.8
0$\bar{7}$1	< 3.1	+ 0.8	02$\bar{4}$	< 2.3	+ 0.7	018	3.9	− 3.0
0$\bar{6}$1	2.9	− 3.1	01$\bar{4}$	20.1	+18.3	028	9.0	+ 7.6
0$\bar{5}$1	< 2.8	− 2.0	004	32.8	−30.6	038	< 3.0	− 0.3
0$\bar{4}$1	22.4	+21.0	014	15.7	+18.3	0$\bar{2}$9	< 3.1	+ 2.7
0$\bar{3}$1	19.4	+19.8	024	26.2	−24.3	0$\bar{1}$9	< 3.1	+ 0.8
0$\bar{2}$1	22.1	+25.1	034	11.7	+10.0	009	5.4	+ 4.3
0$\bar{1}$1	3.6	− 2.7	044	< 2.9	− 1.8	019	3.1	+ 2.4
001	16.7	−16.6	054	< 3.0	+ 2.9	1$\bar{0}$9	3.3	− 3.8
011	10.7	− 9.8	064	4.9	+ 3.9	10$\bar{8}$	6.9	− 5.1
021	25.6	−24.7	074	< 2.9	+ 0.4	10$\bar{7}$	6.9	+ 6.6
031	11.2	−12.9	0$\bar{7}$5	< 3.1	− 1.7	10$\bar{6}$	3.6	− 3.4
041	< 2.6	+ 0.8	0$\bar{6}$5	8.0	+ 8.3	10$\bar{5}$	2.3	+ 4.2
051	4.0	− 6.2	0$\bar{5}$5	< 3.0	+ 1.9	10$\bar{4}$	35.5	+33.5
061	10.4	+12.1	0$\bar{4}$5	< 2.9	− 2.4	10$\bar{3}$	10.9	−12.6
071	< 3.1	− 2.7	0$\bar{3}$5	< 2.7	− 1.4	10$\bar{2}$	15.2	−16.6
081	6.5	+ 6.8	0$\bar{2}$5	16.9	−17.4	10$\bar{1}$	33.8	+31.0
0$\bar{8}$2	< 2.9	+ 1.9	0$\bar{1}$5	< 2.6	+ 0.7	100	32.7	−35.2
0$\bar{7}$2	4.3	+ 6.0	005	3.4	+ 3.7	101	14.3	+13.7
0$\bar{6}$2	2.9	+ 2.0	015	< 2.6	+ 3.4	102	32.6	+42.1
0$\bar{5}$2	12.4	+11.1	025	6.5	+ 5.4	103	5.7	− 5.0
0$\bar{4}$2	9.0	− 9.9	035	2.9	+ 3.8	104	4.7	+ 5.1
0$\bar{3}$2	6.0	+ 5.2	045	3.0	+ 2.9	105	< 3.4	− 0.2
0$\bar{2}$2	24.8	−28.8	055	< 3.1	+ 0.8	106	11.0	−11.9
0$\bar{1}$2	4.5	+ 5.3	065	6.0	− 5.2	107	< 4.1	+ 3.2
002	20.7	−24.6	0$\bar{6}$6	3.1	− 3.1	108	11.1	+ 8.5
012	8.4	− 7.7	0$\bar{5}$6	8.1	− 7.5	2$\bar{0}$9	< 4.8	+ 0.3
022	10.8	− 9.0	0$\bar{4}$6	< 3.0	+ 1.4	20$\bar{8}$	< 4.4	+ 2.1
032	5.5	+ 6.4	0$\bar{3}$6	4.1	− 4.1	20$\bar{7}$	7.1	− 8.1
042	20.1	+19.9	0$\bar{2}$6	12.8	+12.5	20$\bar{6}$	< 3.7	+ 2.3
052	4.1	− 4.9	0$\bar{1}$6	8.0	− 9.6	20$\bar{5}$	13.6	+15.3
062	6.3	+ 6.6	006	21.3	+20.3	20$\bar{4}$	10.1	−10.5
072	3.8	− 4.0	016	6.7	− 6.3	20$\bar{3}$	10.5	+11.3
0$\bar{7}$3	3.1	+ 3.7	026	4.7	+ 4.1	20$\bar{2}$	28.3	+29.5
0$\bar{6}$3	9.0	−11.0	036	4.7	− 5.4	20$\bar{1}$	27.6	−30.2
0$\bar{5}$3	< 2.8	+ 0.7	046	5.3	− 5.6	200	11.6	+10.1
0$\bar{4}$3	8.2	− 9.3	056	< 3.0	+ 0.6	201	4.4	+ 5.2
0$\bar{3}$3	< 2.3	+ 3.2	0$\bar{5}$7	< 3.1	− 2.4	202	14.6	−15.7
0$\bar{2}$3	13.3	−13.3	0$\bar{4}$7	6.1	+ 6.9	203	28.6	+33.6
0$\bar{1}$3	6.5	− 7.0	0$\bar{3}$7	< 3.1	− 0.9	204	7.3	+ 8.2
003	24.2	+21.9	0$\bar{2}$7	6.2	+ 7.6	205	14.5	−11.7
013	11.1	+11.6	0$\bar{1}$7	< 3.0	− 2.3	206	< 4.0	+ 3.9
023	3.3	+ 2.9	007	2.8	− 3.2	207	< 4.3	− 1.5
033	2.6	+ 3.4	017	4.2	− 4.9	208	5.7	− 5.1

Table 2 *(continued)*

| hkl	$|F_o|$	F_c	hkl	$|F_o|$	F_c	hkl	$|F_o|$	F_c
$30\bar{9}$	6.0	+ 4.1	$60\bar{4}$	5.5	+ 4.6	$3\bar{5}0$	11.1	+11.4
$30\bar{8}$	< 4.5	− 2.4	$60\bar{3}$	5.3	+ 4.3	$3\bar{4}0$	4.7	+ 3.0
$30\bar{7}$	5.9	+ 6.6	$60\bar{2}$	< 4.3	− 1.5	$3\bar{3}0$	< 3.0	+ 0.3
$30\bar{6}$	< 4.0	− 2.8	$60\bar{1}$	< 4.3	− 1.7	$3\bar{2}0$	5.5	+ 4.2
$30\bar{5}$	15.5	−15.9	600	5.2	− 4.6	$3\bar{1}0$	10.8	− 9.3
$30\bar{4}$	12.4	+11.2	601	< 4.4	− 0.4	310	4.7	− 4.4
$30\bar{3}$	9.7	+ 9.7	602	4.5	+ 5.1	320	9.6	−10.3
$30\bar{2}$	< 3.0	− 0.4	603	< 4.7	+ 1.6	330	< 3.5	+ 0.8
$30\bar{1}$	27.9	+30.1	604	3.4	+ 3.2	340	< 3.7	− 2.7
300	4.8	− 4.6	$70\bar{3}$	< 4.8	+ 0.7	350	< 3.9	+ 0.4
301	17.7	−18.4	$70\bar{2}$	5.8	+ 4.7	360	3.9	+ 4.8
302	13.4	+12.1	$70\bar{1}$	< 4.7	+ 2.3	$4\bar{8}0$	3.9	+ 3.3
303	5.8	− 7.5	700	< 4.8	− 0.9	$4\bar{7}0$	< 3.9	+ 0.2
304	5.2	− 2.5	701	< 4.9	− 1.8	$4\bar{6}0$	4.9	+ 5.8
305	17.8	+15.7	$1\bar{8}0$	< 3.8	− 1.5	$4\bar{5}0$	8.0	− 8.8
306	4.2	+ 3.7	$1\bar{7}0$	3.9	− 5.6	$4\bar{4}0$	3.5	− 3.1
307	7.1	− 4.4	$1\bar{6}0$	14.1	+13.4	$4\bar{3}0$	< 3.3	− 3.1
$40\bar{8}$	4.7	+ 4.9	$1\bar{5}0$	5.0	− 6.4	$4\bar{2}0$	14.1	−10.7
$40\bar{7}$	5.5	+ 4.6	$1\bar{4}0$	46.8	+46.2	$4\bar{1}0$	< 3.2	− 4.3
$40\bar{6}$	< 4.1	− 0.8	$1\bar{3}0$	11.5	−10.4	410	3.4	+ 3.1
$40\bar{5}$	< 4.0	+ 2.3	$1\bar{2}0$	6.1	+ 5.4	420	8.8	+11.3
$40\bar{4}$	< 3.7	− 1.0	$1\bar{1}0$	11.1	−11.5	430	< 3.7	+ 2.4
$40\bar{3}$	8.6	− 8.1	110	< 2.0	+ 3.1	440	8.4	+ 8.5
$40\bar{2}$	8.5	+ 8.4	120	31.9	−29.9	450	3.9	− 4.5
$40\bar{1}$	4.1	+ 4.2	130	15.4	+18.0	$5\bar{7}0$	< 3.9	− 3.3
400	3.2	− 3.1	140	6.8	+ 6.7	$5\bar{6}0$	4.9	− 3.6
401	17.9	+18.6	150	< 3.7	+ 0.5	$5\bar{5}0$	< 3.9	− 3.2
402	< 3.6	− 0.9	160	< 3.9	+ 2.8	$5\bar{4}0$	< 3.7	+ 0.8
403	11.7	− 9.5	170	< 3.9	+ 0.5	$5\bar{3}0$	5.2	+ 6.2
404	5.6	+ 4.6	$2\bar{8}0$	8.6	+ 7.2	$5\bar{2}0$	8.2	+ 9.9
405	< 4.2	− 2.1	$2\bar{7}0$	< 3.9	+ 0.4	$5\bar{1}0$	< 3.5	+ 2.0
406	< 4.5	− 0.1	$2\bar{6}0$	< 3.7	− 4.0	510	< 3.7	− 3.5
407	9.7	+ 6.4	$2\bar{5}0$	< 3.2	+ 4.3	520	< 3.9	− 3.5
$50\bar{7}$	< 4.7	+ 1.7	$2\bar{4}0$	28.8	−29.8	530	4.0	− 5.2
$50\bar{6}$	4.5	+ 4.4	$2\bar{3}0$	18.4	+20.2	540	3.9	− 3.4
$50\bar{5}$	3.0	+ 2.7	$2\bar{2}0$	27.3	−26.5	$6\bar{6}0$	< 3.9	+ 3.6
$50\bar{4}$	< 4.1	+ 2.3	$2\bar{1}0$	35.4	+31.8	$6\bar{5}0$	< 3.9	0
$50\bar{3}$	< 4.0	− 2.3	210	5.8	− 7.3	$6\bar{4}0$	< 3.9	+ 3.2
$50\bar{2}$	5.5	− 6.4	220	3.0	+ 2.3	$6\bar{3}0$	< 3.9	− 2.4
$50\bar{1}$	< 3.8	+ 0.7	230	4.7	− 3.3	$6\bar{2}0$	4.9	− 6.8
500	8.4	+ 9.0	240	< 3.5	− 0.2	$6\bar{1}0$	< 3.9	− 3.4
501	< 4.0	+ 2.2	250	5.4	− 4.2	610	8.3	+ 8.0
502	< 4.1	+ 2.5	260	3.9	− 5.4	620	< 3.9	− 3.0
503	< 4.2	+ 1.8	270	< 3.8	+ 1.2	$7\bar{4}0$	< 3.9	− 2.2
504	4.4	− 3.9	$3\bar{8}0$	11.7	−10.4	$7\bar{3}0$	6.2	+ 7.1
505	< 4.7	− 0.4	$3\bar{7}0$	9.0	+ 8.5	$7\bar{2}0$	< 4.0	− 1.7
$60\bar{6}$	< 4.8	− 0.7	$3\bar{6}0$	7.4	− 8.0	$7\bar{1}0$	7.7	+ 7.2
$60\bar{5}$	4.6	+ 3.4						
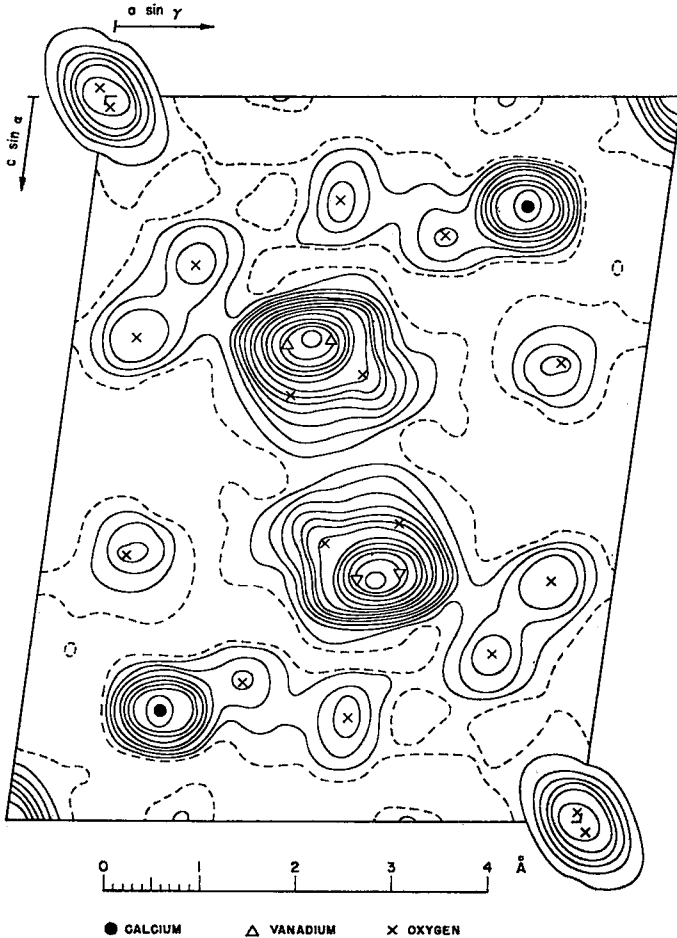
FIG. 2. Final electron-density projection along [010]. Contours at intervals of $2e.\text{Å}^{-2}$ from $8e.\text{Å}^{-2}$ (broken line) to $20e.\text{Å}^{-2}$, and at intervals of $5e.\text{Å}^{-2}$ above $20e.\text{Å}^{-2}$.

DESCRIPTION OF THE STRUCTURE[2]

Projections of the structure along [100] and [010] are shown in Figs. 4 and 5, respectively. Interatomic distances within the oxygen co-ordination polyhedra around the cations Ca, V_1, and V_2 are given in Table 3,

[2]In the text, tables, and Fig. 6, an asterisk denotes an atom in a cell adjacent to the reference cell outlined in the projections of Figs. 1 to 5, inclusive, and in the text, tables and figures a prime identifies an atom which is equivalent by virtue of a centre of symmetry (thus, Ca, Ca′).
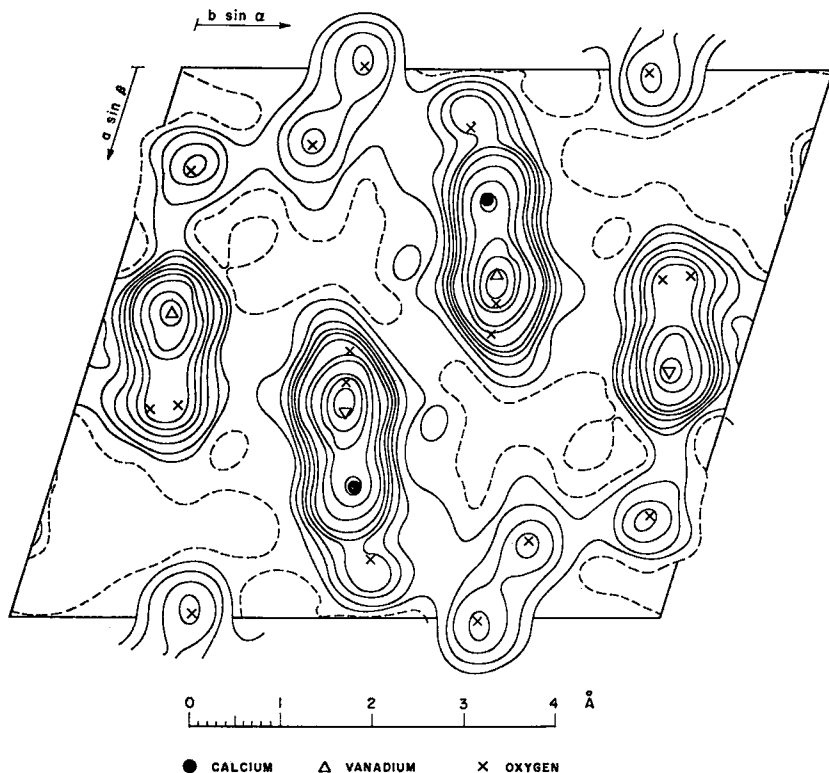
FIG. 3. Final electron-density projection along [001]. Contours at intervals of $2e.\text{Å}^{-2}$ from $8e.\text{Å}^{-2}$ (broken line) to $20e.\text{Å}^{-2}$, and at intervals of $5e.\text{Å}^{-2}$ above $20e.\text{Å}^{-2}$.

and values of the angles O-Ca-O and O-V-O in the various polyhedra are listed in Table 4.

The structure is built up of two kinds of puckered chains. Vanadium co-ordination polyhedra share edges O_1^*-O_1', O_1'-O_2, O_2-O_2', O_2'-O_1 (see Fig. 4) to form double chains of V_1, V_2, V_1', V_2' polyhedra parallel to [010]. These chains are linked though the edges O_2-O_6, O_2-O_7 on one side and through O_2'-O_6', O_2'-O_7' on the other side, as well as through the corners O_4 and O_7' of the V_2-polyhedron, to calcium co-ordination polyhedra which themselves share edges O_7-$O_7'^*$, O_8^*-$O_8'^*$ (see Fig. 5) to form chains parallel to [100].

Each of the two independent atoms of vanadium (V_1, V_2) per cell is surrounded by five atoms of oxygen at the corners of a distorted trigonal bipyramid as illustrated by the stereograms reproduced in Fig. 6A, B. The calculated distance from V_1 to the plane of O_1', O_5, O_6 and from V_2 to
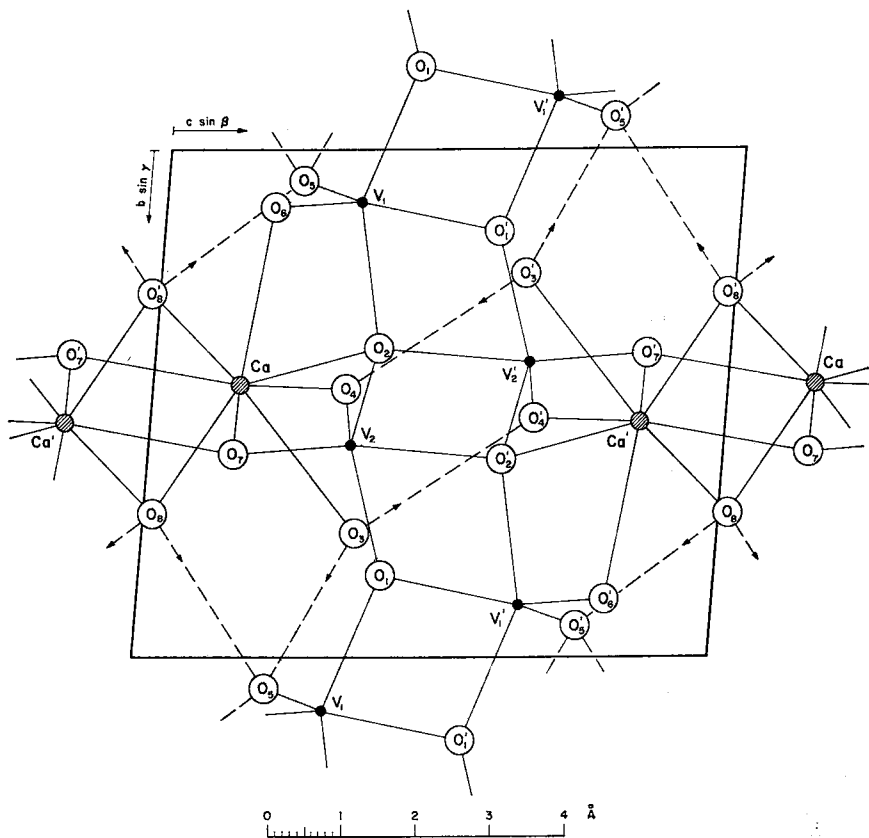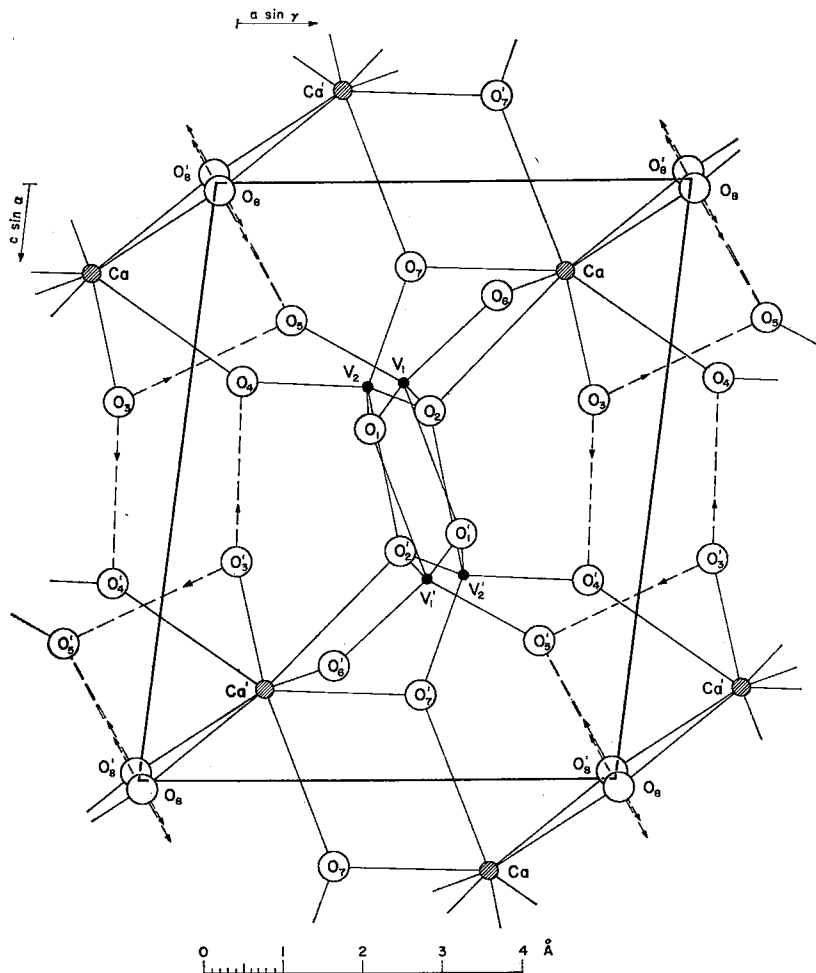
FIG. 4. Projection of the structure along [100]. Broken lines indicate long hydrogen bonds; arrowheads point away from H_2O molecules.

the plane of O_2', O_4, O_7 is only 0.06 Å in each case so that, within the limits of experimental error, each vanadium atom is co-planar with the three oxygen atoms around it. In each case, however, V is displaced away from the centre of the triangle of oxygen atoms towards an edge (V_1 towards O_5-O_6; V_2 towards O_4-O_7) so that short distances (1.62 Å to 1.67 Å) for V_1-O_5, V_1-O_6, V_2-O_4, V_2-O_7 are the result (see Table 3). The two remaining oxygen atoms of each bipyramid (O_1^*, O_2; O_1, O_2) are situated on opposite sides of this plane in positions such that V_1-O_1^*, V_1-O_2, V_2-O_1, V_2-O_2 make acute angles (74° to 78°, see Table 4) with the longest V-O bonds (V_1-O_1', V_2-O_2', see Table 3) in the plane. The vanadium polyhedra are linked through shared edges which are relatively short, thus, $V_1'^*$ to V_1 through O_1^*-$O_1' = 2.50$ Å, V_1 to V_2' through O_1'-$O_2 = 2.44$ Å, V_2' to V_2 through O_2-$O_2' = 2.37$ Å, and V_2 to V_1' through O_2'-$O_1 = 2.44$ Å.

FIG. 5. Projection of the structure along [010]. Broken lines indicate long hydrogen bonds; arrowheads point away from H_2O molecules.

The distances apart of the vanadium atoms across these shared edges are 3.08 Å ($V_1'*$ to V_1), 3.12 Å (V_1 to V_2'; V_2 to V_1'), and 3.16 Å (V_2' to V_2). In each bipyramid the shared edges are those from the apices to the same oxygen atom of the "equatorial" triangle (see Fig. 4); the vanadium atom is displaced in the plane of the triangle away from these edges and the distance between the vanadium atom and the oxygen atom is greater than any other V-O distance in the bipyramid (see V_1-O_1' and V_2-O_2', Table 3). The polyhedra also share the corners O_2 (between V_1 and V_2)

TABLE 3. INTERATOMIC DISTANCES (Å) IN THE CO-ORDINATION POLYHEDRA. (Asterisks, atoms in cells adjacent to that of the cation; Parentheses, edges shared between two V-polyhedra or two Ca-polyhedra; Square Brackets, edges shared between a V-polyhedron and a Ca-polyhedron.)

	O'_1	O_1^*	O_2	O_5	O_6		O'_2	O_1	O_2	O_4	O_7
V_1	2.02	1.94	1.98	1.63	1.67	V_2	2.12	1.84	1.82	1.64	1.62
O'_1		(2.50)	(2.44)	3.42	3.09	O'_2		(2.44)	(2.37)	2.93	3.63
O_1^*				2.63	2.92	O_1				2.71	2.71
O_2				2.72	[2.68]	O_2				2.76	[2.52]
O_5					2.68	O_4					2.62

	O_2	$O_7'^*$	O_6	O_7	O_3	$O_8'^*$	O_4^*	O_8^*
Ca	2.50	2.40	2.43	2.48	2.48	2.59	2.44	2.40
O_2			[2.68]	[2.52]	2.88		3.61	
$O_7'^*$			3.39	(2.95)		3.06		3.10
O_6						2.92	3.37	
O_7					2.90			3.73
O_3							2.83	3.00
$O_8'^*$							2.88	(3.10)

and O_1 (between V_2 and V_1^*) at the apices of the bipyramids, but the distances apart of the vanadium atoms across these shared corners are much greater (V_1 to V_2 across O_2, 3.55 Å; V_2 to V_1^* across O_1, 3.58 Å) than are those across the shared edges. Finally, it may be noted by reference to Figs. 4 and 5 that the equatorial planes of the bipyramids (V_1, O'_1, O_5, O_6; V_2, O'_2, O_4, O_7) are very nearly related by a pseudo-mirror plane normal to [010], and that the ribbon-like band of linked vanadium-oxygen bipyramids lies with its length and width nearly in the (10$\bar{1}$) plane.

Each calcium atom is co-ordinated with eight oxygen atoms, at distances of 2.40 Å to 2.59 Å (see Table 3), situated at the corners of a distorted square antiprism as illustrated by the stereogram in Fig. 6C. The corners of the "square" faces are occupied by O_2, O_7, $O_7'^*$, O_6 and by O_3, O_8^*, $O_8'^*$, O_4^*, and one edge of each face (O_7-$O_7'^*$, O_8^*-$O_8'^*$) is shared between a Ca and a Ca$'^*$ antiprism with Ca to Ca$'^*$ distances of 3.88 Å and 3.91 Å, respectively, across these edges. Two other edges (O_2-O_6, O_2-O_7) of one of the "square" faces are shared with a V_1 and a V_2 bi-pyramid, respectively, and these edges are longer (O_2-O_6, 2.68 Å; O_2-O_7, 2.52 Å) than any of those shared between two vanadium bipyramids. On the other hand, the O_2-O_7 edge is shorter than any of the unshared edges of the V_2 bipyramid and the O_2-O_6 edge is not appreciably longer than the shortest unshared edge of the V_1 bipyramid, while both edges are significantly shorter than any other edges of the Ca antiprism (see Table 3). The separation of Ca from V_1 across O_2-O_6 is 3.30 Å and that

TABLE 4. BOND ANGLES (°) IN THE VANADIUM AND CALCIUM POLYHEDRA

$O_1^*-V_1-O_1$		$O_1-V_2-O_2'$	76
O_2-V_1-O		$O_2-V_2-O_2'$	74
$O_1^*-V_1-$		$O_1-V_2-O_7$	102
$O_1^*-V_1-$	108	$O_1-V_2-O_4$	102
$O_2-V_1-O_5$	97	$O_2-V_2-O_7$	94
$O_2-V_1-O_6$	94	$O_2-V_2-O_4$	106
$O_1'-V_1-O_5$	138	$O_2'-V_2-O_7$	151
$O_1'-V_1-O_6$	113	$O_2'-V_2-O_4$	102
$O_5-V_1-O_6$	108	$O_7-V_2-O_4$	107
$O_1^*-V_1-O_2$	151	$O_1-V_2-O_2$	142
O_2-Ca-O_6	66	$O_7'^*-Ca-O_8'^*$	76
O_2-Ca-O_7	61	$O_7'^*-Ca-O_8^*$	81
$O_7'^*-Ca-O_6$	89	O_3-Ca-O_7	72
$O_7'^*-Ca-O_7$	74	$O_8'^*-Ca-O_6$	71
$O_3-Ca-O_4^*$	70	$O_7-Ca-O_8^*$	100
$O_3-Ca-O_8^*$	76	$O_6-Ca-O_4^*$	88
$O_8'^*-Ca-O_4^*$	70	$O_2-Ca-O_8^*$	145
$O_8'^*-Ca-O_8^*$	77	$O_2-Ca-O_8'^*$	135
$O_2-Ca-O_7'^*$	117	$O_7'^*-Ca-O_3$	134
O_6-Ca-O_7	107	$O_7'^*-Ca-O_4^*$	145
$O_3-Ca-O_8'^*$	134	$O_7-Ca-O_8'^*$	150
$O_4^*-Ca-O_8^*$	83	$O_7-Ca-O_4^*$	140
O_2-Ca-O_3	71	O_6-Ca-O_3	129
$O_2-Ca-O_4^*$	94	$O_6-Ca-O_8^*$	148

of Ca from V_2 across O_2-O_7 is 3.25 Å. Finally, the Ca antiprisms are linked to the V_2 bipyramids in the [100] direction by the shared corner O_4 while the Ca' antiprisms are linked to the same V_2 bipyramids in the [001] direction by the shared corner O_7; the Ca* to V_2 distance across O_4 is 3.80 Å and the Ca'* to V_2 distance across O_7 is 3.79 Å.

The Water Molecules

Several facts indicate that in both rossite and metarossite the water is present in the crystal structure as H_2O molecules. Thus the dehydration of rossite to metarossite is discontinuous, virtually all water is driven off at about 120° C, the two hydrates and the dehydrated material are soluble in water (although with increasing difficulty from rossite to the anhydrous vanadate), and rossite crystallizes from aqueous solutions of rossite, metarossite, or the anhydrous material (Foshag & Hess, 1927).

Since Ca^{2+} ions are hydrated in aqueous solution and metarossite easily loses its water of crystallization, it is to be expected that the H_2O molecules probably are co-ordinated in the crystal structure with the cation rather than with the metavanadate anion. Consideration of the cations closely associated with each of the eight oxygen atoms in the asymmetric unit of metarossite (Table 5) shows that O_1 is co-ordinated with three vanadium atoms (V_1^*, V_1', V_2), O_2 is co-ordinated with one
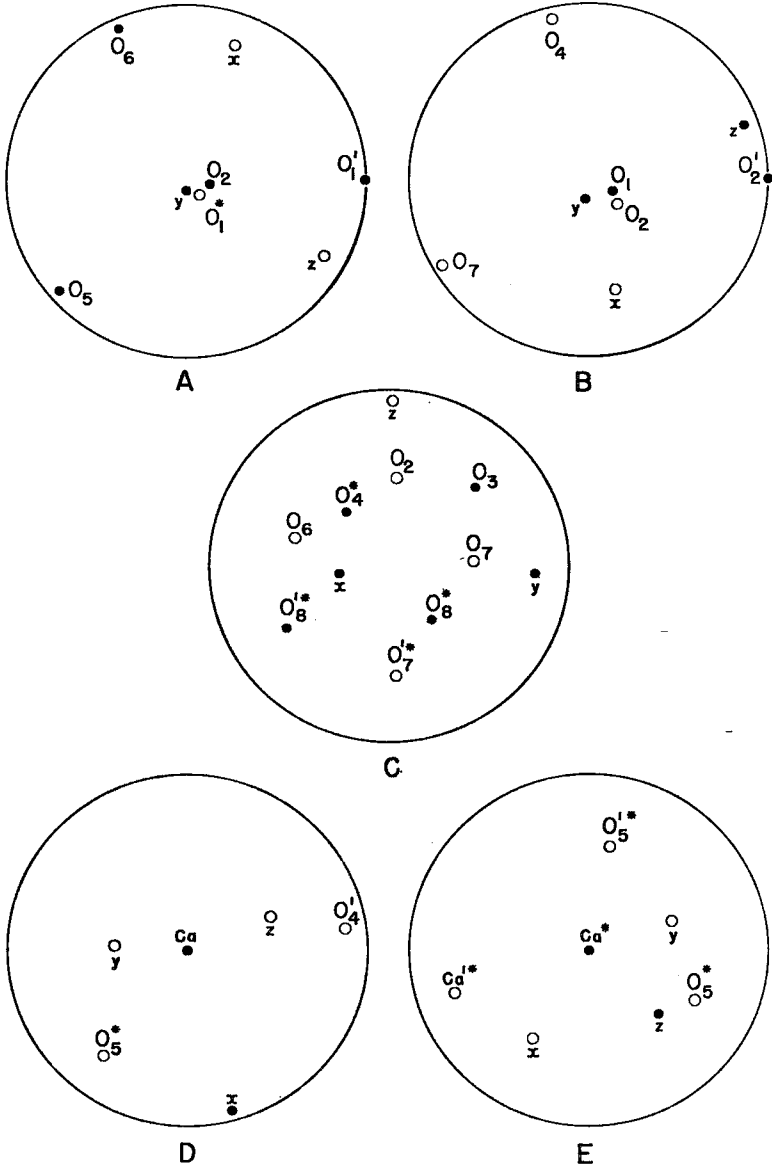
FIG 6. Stereographic projections of the environment of (A) V_1, (B) V_2, (C)C. a, (D) O_3, (E) O_8.

TABLE 5. NEAREST NEIGHBOURS OF THE OXYGEN ATOMS.
(Italics indicate short V–O distances)

O_1	V_1*	V_1'	V_2					
O_2	V_1	V_2	V_2'	Ca				
O_3				Ca		O_4'	O_5*	
O_4	V_2			Ca*	O_3'			
O_5	V_1					O_3*	O_8*	$O_8'*$
O_6	V_1			Ca				
O_7	V_2			Ca	Ca'*			
O_8				Ca*	Ca'*	O_5*	$O_5'*$	

calcium atom and three vanadium atoms (Ca, V_1, V_2, V_2'), and O_7 is not only co-ordinated with two calcium atoms and one vanadium atom (Ca, $Ca'*$, V_2) but the O_7-V_2 bond is relatively short (1.62 Å). It is reasonable to assume, therefore, that the electrostatic valencies of O_1, O_2, and O_7 must be fully satisfied by their neighbouring cations and that these oxygen atoms cannot represent H_2O molecules.

Of the other five oxygen atoms, O_4 and O_6 are each co-ordinated with one calcium atom and one vanadium atom (O_4 with $Ca*$, V_2; O_6 with Ca, V_1), O_8 is co-ordinated with two calcium atoms ($Ca*$, $Ca'*$), O_3 is co-ordinated only with Ca, and O_5 is co-ordinated only with V_1. Now O_6 has no close oxygen neighbours (apart from those co-ordinated with the same vanadium atom) and it is rather closely bound to V_1 (O_6-V_1, 1.67 Å), so that it is improbable that O_6 represents a water molecule.

Furthermore, there are only four relatively short distances of less than 3.05 Å among oxygens not co-ordinated with the same cation. These distances are 2.92 Å for O_3-O_4', 2.88 Å for O_3-O_5^*, 2.78 Å for O_5^*-O_8, and 2.89 Å for O_5-$O_8'^*$, and are of the appropriate order of magnitude for a "long" hydrogen bond ($O \cdot H \cdots O$), along the direction of which H is more closely associated with one O than with the other (Megaw, 1952). Of these, only O_3, O_5 and O_8 are involved in two such bonds and therefore two of these must represent the water molecules. O_5 can be eliminated for it is closely bound to V_1 and there is no precedent for vanadium having a water molecule as a near neighbour; it is moreover unlikely on the grounds of electrostatic valency considerations. O_3 and O_8 must therefore represent the water molecules.

Taking as a guide the concept of a water molecule as an oxygen at the centre of a tetrahedral distribution of two negative and two positive charges, the two negative charges of O_3 would be directed towards Ca with one H^+ linking O_3 to O_4' and the other linking O_3 to O_5^*. O_8 would be linked to O_5^* through one H^+ and to $O_5'^*$ through the other, while the two negative charges would co-ordinate O_8 to $Ca*$ and to $Ca'*$. The environments of O_3 and O_8 are shown in Fig. 6D, E.

The co-ordination of O_3 is three-fold (distorted planar) with distances O_3-Ca of 2.48 Å, O_3-O_5^* of 2.88 Å, O_3-O_4' of 2.92 Å. The angle O_5^*-O_3-O_4' is 131°. O_3 is out of the plane of the triangle Ca, O_4', O_5^* by 0.82 Å and the sides of the triangle are 4.00 Å for Ca-O_4', 4.31 Å for Ca-O_5^*, and 5.28 Å for O_5^*-O_4'. It may be noted that the cations (other than Ca) which are closest to O_3 are V_1' and V_2 but the interatomic distances (O_3-V_1', 3.46 Å; O_3-V_2, 2.92 Å) are too long to represent anything more than Van der Waals contacts. This is reminiscent of the environment of the water molecule, O_9, in afwillite (Megaw, 1952).

The co-ordination of O_8 is four-fold with Ca*, Ca'*, O_5^*, O'^*_5 at the corners of a distorted tetrahedron with distances O_8-Ca* of 2.40 Å, O_8-Ca'* of 2.59 Å, O_8-O_5^* of 2.78 Å, O_8-$O_5'^*$ of 2.89 Å, and with the angles listed in Table 6.

TABLE 6. ANGLES (°) IN THE O_8-TETRAHEDRON.
(Arrowheads indicate directions of "long" hydrogen bonds.)

O_5^*	$\leftarrow O_8 \rightarrow$	$O_5'^*$	91
O_5^*	$\leftarrow O_8 -$	Ca*	112
O_5^*	$\leftarrow O_8 -$	Ca'*	124
Ca*	$- O_8 \rightarrow$	$O_5'^*$	118
Ca'*	$- O_8 \rightarrow$	$O_5'^*$	108
Ca*	$- O_8 -$	Ca'*	103

DISCUSSION

When oxygen co-ordination polyhedra around vanadium share edges as in metarossite the forces of repulsion between multivalent V are sufficiently strong to displace the vanadium atoms away from the shared edges and cause a reduction in the lengths of these edges. This effect is not observed, however, in the case of those edges of the square antiprisms around the weaker divalent Ca which are shared between two calcium atoms. The average length of the sixteen O-O edges of the antiprism is 3.06 Å of which two are shared with another Ca; the mean of these two is 3.02 Å. The effect of V, however, is shown by the average length of the O-O edges shared between Ca and V which is reduced to 2.60 Å and may be compared with the still smaller mean value of 2.44 Å for those edges shared between two vanadium bipyramids.

The eight-fold oxygen co-ordination around Ca in the form of a square antiprism is not unexpected from a radius-ratio viewpoint (Wells, 1950, p. 90) in spite of the distortion introduced by the presence of vanadium, and the five-fold oxygen co-ordination around V_1 and V_2 now appears to be characteristic of at least some of the metavanadates. The soft, friable nature of metarossite may be attributed to the relative weakness both

of the Ca-O bonds and the "long" hydrogen bonds, and the habit parallel to {10Ī} to the fact that the bands of vanadium-oxygen bipyramids lie approximately in this plane.

As is apparent from Fig. 4 the shared edge O_8-O_8'* between the calcium polyhedra is approximately parallel to [010] and, from Fig. 5, the plane containing these two oxygen atoms and the calcium atoms of the linked polyhedra is almost perpendicular to (10Ī). Furthermore, as already mentioned, the band of linked vanadium polyhedra has its length and width nearly in (10Ī). Thus the observed twinning, with {10Ī} as the twin-plane, is readily accounted for in terms of reflection across (10Ī) as a pseudo-mirror plane; this would entail very little rearrangement of the atoms in the immediate vicinity of the twin-plane.

Tetrahedral co-ordination of oxygen atoms around vanadium is found in the orthovanadates where it may be more or less regular as in pyro-belonite, $PbMn(VO_4)(OH)$ (Donaldson & Barnes, 1955a), in bracke-buschite, $Pb_2(Mn,Fe)(VO_4)_2.H_2O$ (Donaldson & Barnes, 1955b), and almost certainly in descloizite, $Pb(Zn,Cu)(VO_4)(OH)$ (Qurashi & Barnes, 1954), or irregular as in pucherite, $BiVO_4$ (Qurashi & Barnes, 1953) and in vanadinite, $Pb_5(VO_4)_3Cl$ (Trotter & Barnes), 1958). In addition to two V-O bonds of 1.95 Å and two of 1.76 Å in pucherite there are two additional oxygen atoms at 2.69 Å from V so that the distribution of oxygen atoms around the vanadium atoms in this structure may be considered to represent a transition from the ideal four-fold co-ordination of the other orthovanadates towards six-fold co-ordination.

The polyvanadate, $K_3V_5O_{14}$, contains some tetrahedrally co-ordinated vanadium (Byström & Evans, 1959). The tetrahedra are regular with V-O distances of about 1.65 Å. Another oxygen approaches one face of each tetrahedron to give a V-O distance of 3.4 Å. The co-ordination might possibly be considered as a first stage in the transition from tetra-hedral to trigonal bipyramidal co-ordination. This compound also contains five-fold co-ordinated vanadium with the oxygens lying at the apices of an approximately square pyramid. Again, a further oxygen approaches to within 3.4 Å of the vanadium measured across the base of the pyramid and this might indicate a first step towards octahedral co-ordination.

The five-fold trigonal bipyramidal co-ordination in metarossite, $Ca(VO_3)_2.2H_2O$, occurs also in $KVO_3.H_2O$ (Christ, Clark & Evans, 1954), and in the non-stoichiometric pentavalent vanadium oxides (oxygen vanadium bronzes) β-$Na_{2-x}V_6O_{15}$ (Wadsley, 1955; Ozerov, Gol'der & Zhdanov, 1957), γ-$Li_{1+x}V_3O_8$ (Wadsley, 1957), $K_{0.33}V_2O_5$ (which corres-ponds to $K_{2-x}V_6O_{15}$, Ozerov, Gol'der & Zhdanov, 1957), although the bipyramids in metarossite lack the equatorial planes of symmetry in the

corresponding polyhedra of the other structures. This difference is slight, however, and is due to relatively small displacements of some of the oxygen atoms. In all five structures the bipyramids share two edges, from their apices to one corner of the equatorial triangle, to form puckered chains, and the vanadium atoms are displaced away from the shared edges to make close contacts with the two oxygen atoms of the triangle which are not involved in chain formation. In metarossite the repeat length of the vanadium-oxygen chains is 7.06 Å as compared with about 3.6 Å in the other four structures. For comparison purposes the V-O distances within the various trigonal bipyramids are given in Table 7; the differences between the two short bonds in the non-stoichiometric oxides may be significant but probably is not so in either potassium metavanadate monohydrate or in metarossite. The great length of the long bond in the equatorial triangle (see Table 7), which if ruptured would result in chains of very distorted tetrahedra linked by corners, may be considered as a faint vestige of four-fold co-ordination. On the other hand, the five-fold co-ordinated atoms of vanadium in β-Na$_{2-x}$V$_6$O$_{15}$, in

TABLE 7. V-O DISTANCES (Å) IN THE TRIGONAL BIPYRAMIDS OF VARIOUS STRUCTURES.
(The first three values in each case are for distances in the equatorial plane of the bipyramid.)

β-Na$_{2-x}$V$_6$O$_{15}$	γ-Li$_{1+x}$V$_3$O$_8$	K$_{0.33}$V$_2$O$_5$	KVO$_3$.H$_2$O	Ca(VO$_3$)$_2$.2H$_2$O	
1.56	1.60	1.55	1.63	1.63	1.62
1.78	1.78	1.79	1.67	1.67	1.64
2.00	2.06	2.00	1.99	2.02	2.12
1.91	1.88	1.89	1.93	1.94	1.82
1.91	1.88	1.89	1.93	1.98	1.84
±0.05	±0.03	—	±0.02	*e.s.d.,* 0.03	

γ-Li$_{1+x}$V$_3$O$_8$, and in K$_{0.33}$V$_2$O$_5$ are separated from a sixth atom of oxygen by 2.68 Å, 2.86 Å, and 2.68Å, respectively, which Wadsley (1955, 1957) and Ozerov, Gol'der & Zhdanov (1957) have pointed out may be considered as the result of lengthening one V-O bond in a six-fold (octahedral) polyhedron. As mentioned in the discussion of O$_3$ as representing one of the H$_2$O molecules in metarossite, O$_3$ is 3.46 Å from V$_1$, and O$_3'$ is 2.92 Å from V$_2$, so that the latter, at least, may also be considered in a similar light.

In addition to the vanadium atoms already discussed, β-Na$_{2-x}$V$_6$O$_{15}$, γ-Li$_{1+x}$V$_3$O$_8$, and K$_{0.33}$V$_2$O$_5$ each contains two other crystallographically distinct atoms of vanadium which are co-ordinated with six oxygen atoms in the form of distorted octahedra (V-O, 1.56 to 2.36 Å) in which one V-O bond, although relatively long, is appreciably shorter than the sixth V-O distance mentioned in the last paragraph. Similarly distorted octahedra occur in V$_{12}$O$_{26}$ (Aebi, 1948; V-O, 1.85 to 2.50 Å) while more

regular octahedra are found in montroseite, $(V,Fe)O(OH)$ (Evans & Block, 1953; V-O, 1.94 to 2.10 Å); paramontroseite, VO_2 (Evans & Mrose, 1955; V-O, 1.88 to 2.13 Å); and apparently in doloresite, $3V_2O_4.4H_2O$, duttonite, $V_2O_4.2H_2O$, and häggite, $V_2O_3.V_2O_4.3H_2O$ (Evans & Mrose, 1958), for which final structural details have not yet been published. These octahedra share edges with two or more other octahedra to give various types of chains. The vanadium is displaced away from these shared edges so that, if the long bonds are omitted, the resulting co-ordination polyhedra share corners rather than edges. Duttonite contains single chains of octahedra formed by each octahedron sharing two opposite edges. Each vanadium is displaced away from the centre of its octahedron of oxygens, so that those in neighbouring octahedra oppose one another. In doloresite where similar single chains alternate with double ones this does not occur; presumably because the vanadium atoms in the double chains are displaced towards the oxygens which link them to the single chains. Nearly regular octahedral co-ordination of oxygen atoms around vanadium occurs in the spinels ZnV_2O_4 and MgV_2O_4 and in the inverse spinel VMg_2O_4 (Rüdorff & Reuter, 1947).

The problem of vanadium pentoxide has been omitted intentionally from this discussion because a re-examination of its structure by three-dimensional methods is at present underway in this laboratory. Structures have been proposed by Ketelaar (1936) and by Byström, Wilhelmi & Brotzen (1950) which differ in space group ($Pmn2_1$; $Pmnm$) and, to some extent, in the atomic parameters.

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