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The Crystal Structure of Pascoite, $Ca_3V_{10}O_{28} . 17H_2O$

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The crystal structure of pascoite, $Ca_3V_{10}O_{28} . 17H_2O$, has been determined from Patterson and Fourier syntheses with the use of three-dimensional counter data for 1984 observed reflections. Refinement has been carried out by differential and least-squares methods in space groups $I2$ and $I2/m$ to a final R index of 0·05 in each. The cell constants are $a=16·834$, $b=10·156$, $c=10·921$ Å, $\beta=93°\ 8'$. The final difference maps favour $I2$ with an ordered structure in which one of the calcium atoms is coordinated to seven H_2O molecules, rather than a disordered structure in $I2/m$ with equal probability of six- and eight-coordinated H_2O molecules around the calcium atom. The two other calcium atoms are each linked to the decavanadate group through two apical oxygen atoms on opposite sides of the group and each is also coordinated to five H_2O molecules. The decavanadate group, $V_{10}O_{28}$, has orthorhombic *mmm* symmetry, consists of ten VO_6 octahedra sharing edges, and is basically the same as that in the zinc analogue of hummerite, $K_2Zn_2V_{10}O_{28} . 16H_2O$. The complex $[(Ca . 5H_2O)_2V_{10}O_{28}]^{2-}$ ions in the structure are linked to one another and to the $[Ca(H_2O)_7]^{2+}$ ions by hydrogen bonds only.

Introduction

Pascoite, from Minasragra, Peru, was first described by Hillebrand, Merwin & Wright (1914) as probably monoclinic with the formula $2CaO . 3V_2O_5 . 11(?)H_2O$; it has since been found in the vanadium–uranium ore deposits of the Colorado Plateaus (Weeks & Thompson, 1954). In nature it is leached out of vanadium oxide ores by surface waters. It is readily synthesized in the laboratory by leaching calcium and vanadium oxides with water to produce a slightly acid (*p*H 4–6), orange solution from which good, orange-red crystals are obtained by evaporation at room temperature. The natural mineral itself also may be recrystallized from water. Powder patterns prove the identity of the natural and laboratory-prepared material. Evans, Mrose & Marvin (1955), and Marvin & Magin (1959) have shown that synthetic and natural pascoite have the composition $Ca_3V_{10}O_{28} . 16–17H_2O$, and have classified pascoite as a true decavanadate. According to Marvin & Magin (1959) the uncertainty in the water content arises from the fact that 17 molecules per formula unit is in better agreement with the analytical results, while 16 agrees best with the density measurements which, however, are not given. They also state that 'the exact amount of water will not be known until the crystal structure has been determined'. Rossotti & Rossotti (1956) have shown that the decavanadate ion, $V_{10}O_{28}^{6-}$, *in solution* must be a 10-nucleate molecular group. The complete structure of this group has now been determined for the first time by the present crystal-structure investigation of pascoite, and by an entirely independent, and simultaneous, analysis of the structure of $K_2Zn_2V_{10}O_{28} . 16H_2O$ (Evans, 1966), which is the zinc analogue of the mineral hummerite, $K_2Mg_2V_{10}O_{28} . 16H_2O$ (Evans, Swallow & Barnes, 1964).

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Crystal data

Berman in 1942 (Palache, Berman & Frondel, 1951) reported triclinic unit cell data for pascoite, but Evans, Mrose & Marvin (1955), Mrose (1955), Barnes (1960), and Bachmann (1961) are unanimous in finding the crystal to be monoclinic with unit-cell constants in good mutual agreement within the accuracy of the experimental methods (Weissenberg, powder, precession) employed, and with systematic extinctions of $h+k+l=2n+1$ characteristic of space groups $I2$, Im, and $I2/m$. The body-centered lattice adopted by Evans, Mrose & Marvin (1955), instead of an end-centered one ($C2$, Cm, $C2/m$, nos. 5, 8, 12, *International Tables for X-ray Crystallography*, 1952), has been retained in the present investigation because the unit cell then has a β angle very much closer to 90°.

The present cell constants are based on measurements of the 2θ values of high-angle axial reflections obtained with a General Electric XRD-5 scintillation-counter diffractometer, a take-off angle of 1°, slits of 0·02° and 0·05°, and Cu radiation (λ, $K\alpha_1=1·54050$ Å, $K\alpha_2=1·54434$ Å).

Pascoite is monoclinic with $a=16·834$ ($\sigma=0·003$), $b=10·156$ ($\sigma=0·002$), $c=10·921$ ($\sigma=0·002$) Å, $\beta=93°8'$ ($\sigma=3'$), $U=1864·34$ Å^3, F.W. 1384·012 (for 17 H_2O), D_m (flotation in methyl iodide, benzene, carbon tetrachloride) $=2·45_5$ g.cm^{-3} at 21°C, $Z=2$, $D_c=2·465$ g.cm^{-3} (for $17H_2O$), μ(Cu) $=261$ cm^{-1}, μ(Mo) $=12·6$ cm^{-1}, $F(000)=1368$ (for $17H_2O$).

Because of the reported ambiguity in the water content (Marvin & Magin, 1959) a redetermination was carried out in this laboratory on 1 to 2 g samples of pascoite prepared by the addition of excess vanadium pentoxide to a suspension of calcium hydroxide in boiling water until the solution became orange in colour, followed by immediate filtration, and crystallization (by cooling and evaporation) of the filtrate. The orange-red crystals were recrystallized from distil-

led water and dried in air at 40°C. Five determinations of the water lost after fusion varied from 22·30 to 22·62% (mean 22·46%). Two samples, therefore, were first dried *to constant weight* at 45°C; the water subsequently lost after fusion amounted to 22·11 and 22·13% (mean 22·12%): calculated for $16H_2O$, 21·10%, for $17H_2O$, 22·13%, and found by Marvin & Magin (1959), method not given, 22·23%. The density calculated on the basis of the present unit cell constants is 2·433 g.cm^{-3} for $16H_2O$ and 2·465 g.cm^{-3} for $17H_2O$; measured, $2{\cdot}45_5$ g.cm^{-3}. The corresponding values calculated with the cell constants of Evans, Mrose & Marvin (1955) are 2·417 and 2·449 g.cm^{-3} respectively; measured values were not given (Evans, Mrose & Marvin, 1955; Marvin & Magin, 1959). It is also of interest to note that Hillebrand, Merwin & Wright (1914, p.49) state that 'The specific gravity is about 2·457'. All of the available evidence, therefore, strongly supports the conclusion that the formula for pascoite is $Ca_3V_{10}O_{28}.17H_2O$. It will be shown later that this is confirmed by the crystal structure analysis.

Data collection

The crystal employed for data collection was selected from a sample of the synthetic crystals recrystallized from water on a microscope slide. It was approximately equidimensional, about 0·1 mm in linear dimensions, and was mounted with **b** along the φ axis of the goniostat. Intensity data were measured with Mo $K\alpha$ radiation (Nb filter), a scintillation counter with open window, a take-off angle of 2°, and the 2θ, θ scan method (Furnas, 1957). The background was determined separately at each reciprocal-lattice site and was subtracted from the total count. All the very strong and very weak reflections, and many of those of medium intensity, were measured several times. All 4238 possible reflections within the range $\sin\theta/\lambda < 0{\cdot}8$ were examined, but only 1984 produced counts above threshold values. The appropriate 1/Lp corrections were applied to the net intensities, but no corrections for absorption were considered necessary. The mean angular mosaic spread along the directions of the three crystallographic axes was very small ($\sim 0{\cdot}25°$). The intensity of the 600 reflection was recorded at short time-intervals throughout the data collection to provide a standard for placing all data on the same relative scale.

Structure determination and refinement

A three-dimensional Patterson synthesis, computed with the F^2's for the observed reflections after the application of zero-level 1/Lp values as a sharpening function, showed that the Harker section at $V=0$ was densely populated whereas there was only one peak of medium height on the Harker line at $U=0$, $W=0$. These features strongly indicated that the space group was $I2$ (or $I2/m$ if many of the atoms were on the mirror plane at $y=0$) and not Im. The implication diagram was constructed from the $P(U,0,W)$ section, and its ambiguity (reduced from 4 to 2 by the body-centring) was solved by searching the other sections for the unsymmetrical peaks (Buerger, 1959). The coordinates of all V, all Ca, and three O atoms of the asymmetric unit were deduced from this diagram. Structure factors were calculated in $I2$ with the coordinates of these atoms only, and a Fourier synthesis was computed with the F's for which the phases appeared to be reliable. At this stage the formula for pascoite with $16H_2O$ per formula unit had not come into question, and it was possible to locate all remaining O atoms with reasonable certainty. The decavanadate group showed up as a condensed system of ten VO_6 octahedra sharing edges, with two calcium atoms each linked to a pair of apical oxygen atoms, on opposite sides of the group, and to five other oxygen atoms (H_2O molecules), and with the third calcium atom apparently octahedrally coordinated to six other oxygen atoms (H_2O molecules) as a separate hydrated ion (Evans, Swallow & Barnes, 1964). The R index was 0·27.

Refinement of this structure, however, progressed rather slowly, and, because the atoms were very nearly related by mirror symmetry across a plane normal to **b**, it became apparent that the space group might in fact be $I2/m$. Least-squares refinement, therefore, was resumed in $I2/m$, anisotropic thermal parameters were adopted for all atoms (except H atoms which were not included in the refinement procedure) and the R index dropped to 0·095. The results, however, were not satisfactory because of a residual peak of 4·1 e.Å^{-3} in the difference map at approximately 2·4 Å from the isolated calcium atom, Ca(2), and because of unreasonably high thermal parameters indicated for one of the oxygen atoms, O(23), attached to Ca(2). Suspiciously high thermal anisotropy also was shown by O(17) and O(18), which are related by mirror symmetry in $I2/m$.

These observations prompted the reappraisal of the water content of pascoite and the conclusion that the more probable formula contained $17H_2O$ and that the space group probably was $I2$. At the same time the intensities of a large number of the reflections, especially the very weak ones, were remeasured to provide improved counting statistics. Several tests with the improved data resulted in Fourier and difference syntheses consistently in favour of the formula $Ca_3V_{10}O_{28}.17H_2O$ and space group $I2$.

Although the structure of the complex ion $[(Ca.5H_2O)_2V_{10}O_{28}]^{2-}$ was clear and unambiguous, there still remained the possibility that, instead of the apparent overall ordered structure with space group $I2$ and the remaining calcium ions all present as $[Ca(H_2O)_7]^{2+}$, the space group might conceivably be $I2/m$ with structural disorder in which $[Ca(H_2O)_6]^{2+}$ and $[Ca(H_2O)_8]^{2+}$ ions might occupy the same sites with equal probability.

Final refinement, therefore, was carried out first for the ordered structure in $I2$ by four cycles of least squares with the use of the 3×3 and 6×6 block-dia-

gonal approximation, a damping factor of 0·5, and a weighting function of the form

$$w=1/\{1+[0\cdot01(KF_o-100)]^2\}$$

where K is the scale factor. The least-squares program was written for the IBM 1620 computer by Dr G.A. Mair (Ahmed, Gabe, Mair & Pippy, 1963). Observed and calculated differential syntheses were computed after each cycle of least squares as a check on the indicated shifts in the positional parameters. Deviations from the $y=0$ plane were accepted only when they were indicated by both methods. In the least-squares refinement some of the oxygen atoms of the decavanadate group moved off this plane by as much as 0·01 Å whereas the differential syntheses showed them exactly in the plane and consequently they were left in this position; their x and z coordinates were taken as the means of the results of the two refinement procedures. Exact mirror symmetry across $y=0$ was accepted only when the two atoms of a pair were related by this symmetry to within ±0·0002 in their fractional coordinates. The final R index for the observed data was 0·050.

The disordered structure was then refined by two cycles of least squares after adjusting all coordinates to conform with $I2/m$. The final R index for the observed data was 0·051, virtually the same as before.

Two final difference maps, one for each structure, therefore, were evaluated. Both were inconclusive regarding the sites of the hydrogen atoms, and both showed almost the same residual electron density, as high as ±0·8 e.Å^{-3}, near the positions of the vanadium atoms. Nevertheless, the remainder of the $I2$ map was almost uniformly flat, whereas the $I2/m$ map showed pronounced residual electron densities at the Ca(2) and O(22) positions indicating that both atoms should be shifted slightly off the mirror plane. Thus, near Ca(2), $\Delta\varrho=-1\cdot38$ e.Å^{-3} at $y=0$ and $\Delta\varrho=+0\cdot52$ e.Å^{-3} at $y=0\cdot07$ Å, while near O(22), $\Delta\varrho=-0\cdot57$ e.Å^{-3} at $y=0$ and $\Delta\varrho=+0\cdot54$ e.Å^{-3} at $y=0\cdot07$ Å.

Experience throughout the refinement procedure and the final difference syntheses strongly support the final conclusion that the formula for pascoite is $Ca_3V_{10}O_{28}\cdot 17H_2O$, the space group is $I2$, the structure is ordered, and consists of separate $[(Ca\cdot 5H_2O)_2V_{10}O_{28}]^{2-}$ and $[Ca(H_2O)_7]^{2+}$ ions.

Atomic scattering-factor curves for V, Ca (attached to the decavanadate group), Ca^{2+} [for the separate ion, Ca(2)], and O were taken from *International Tables for X-ray Crystallography* (1962).

Results and discussion

The fractional atomic coordinates and their e.s.d.'s, computed from the expressions of Cruickshank (1949, 1950) and then raised by 50% to allow for the omission of the unobserved reflections and the absence of a center of symmetry, are given in Table 1. Atoms Ca(2), V(1*a*), V(1*b*), and O(23) are in special positions 2(*a*), and the remainder are in general positions 4(*c*), of space group $I2$. The observed and calculated electron-density maxima, their mean curvatures, and the anisotropic thermal parameters are collected in Table 2. The complete structure-factor table, based on the parameters listed in Tables 1 and 2, has been deposited in the National Science Library of Canada at the National Research Council, Ottawa. A summary of the agreement between $|F_o|$ and $|F_c|$ (Ahmed & Barnes, 1963*a*), however, is presented in Table 3 where it may be noted that only four reflections (all unobserved) out of 4238 examined show relatively high discrepancies.

A projection along [010] of the contents of one unit cell is reproduced in Fig. 1, in which the origin is at the centre of the diagram and the positive direction of the y axis points downwards from the page. The two vanadium atoms on the diad axis have been designated V(1*a*) and V(1*b*) to avoid any possible confusion by the use of V(6) for one of the vanadium atoms in the decavanadate group, $V_{10}O_{28}$, in which the remaining eight vanadium atoms are related in pairs by the diad axis; the symmetrically equivalent atoms of each pair at x,y,z (Table 1) and $\bar{x},y,\bar{z}$ are distinguished by the addition of a prime to the number of the atom at $\bar{x},y,\bar{z}$ [*e.g.* V(3), V(3′)]. In Fig. 1 two concentric circles indicate atoms related by mirror symmetry across the plane at $y=0$; a third concentric, or almost concentric, circle represents an atom with x,z coordinates almost the same as those of the pair at $\pm y$ but with $y=0$, specifically O(1) and O(6). Other atoms, represented by single circles, which also have $y=0$ are V(4), V(5),

Table 1. *Fractional atomic coordinates* (*e.s.d.'s* $\times 10^4$ Å *in parentheses*)

Atom	x	y	z
Ca(1)	0·2655 (9)	0 (9)	0·3618 (10)
Ca(2)	0·5000 (0)	0·0110 (14)	0 (0)
V(1*a*)	0 (0)	0·1635 (6)	0 (0)
V(1*b*)	0 (0)	−0·1635 (6)	0 (0)
V(2)	0·1175 (8)	0·1497 (10)	−0·2071 (9)
V(3)	0·1175 (8)	−0·1497 (10)	−0·2071 (8)
V(4)	0·1596 (6)	0 (7)	0·0343 (9)
V(5)	0·0419 (6)	0 (7)	0·2420 (6)
O(1)	0·0513 (25)	0 (28)	−0·0898 (25)
O(2)	0·0517 (34)	0·2621 (31)	−0·0902 (30)
O(3)	0·0517 (34)	−0·2621 (32)	−0·0902 (31)
O(4)	0·0192 (39)	0·1320 (33)	−0·2947 (33)
O(5)	0·0192 (38)	−0·1320 (34)	−0·2947 (32)
O(6)	0·1549 (32)	0 (44)	−0·2747 (40)
O(7)	0·1572 (52)	0·2662 (53)	−0·2800 (50)
O(8)	0·1572 (54)	−0·2662 (53)	−0·2800 (51)
O(9)	0·1857 (40)	0·1324 (45)	−0·0674 (44)
O(10)	0·1857 (39)	−0·1324 (42)	−0·0674 (44)
O(11)	0·0847 (30)	0·1208 (28)	0·1157 (31)
O(12)	0·0847 (29)	−0·1208 (29)	0·1157 (31)
O(13)	0·2300 (34)	0 (55)	0·1420 (31)
O(14)	0·1195 (32)	0 (44)	0·3360 (32)
O(15)	0·3400 (71)	0·1728 (45)	0·2752 (51)
O(16)	0·3400 (72)	−0·1728 (48)	0·2752 (54)
O(17)	0·2130 (58)	0·1937 (54)	0·4599 (55)
O(18)	0·2258 (84)	−0·1460 (81)	0·5154 (84)
O(19)	0·3819 (82)	0·0017 (66)	0·4961 (100)
O(20)	0·3626 (66)	−0·0103 (96)	−0·0729 (65)
O(21)	0·4245 (85)	0·2034 (62)	0·0565 (81)
O(22)	0·4862 (80)	−0·0218 (91)	0·2165 (56)
O(23)	0·5000 (0)	−0·2203 (60)	0 (0)

Table 2. *Electron densities* (e.Å^{-3}), *principal curvatures* (e.Å^{-5}), *and anisotropic thermal parameters* ($\times 10^5$) *for the expression* $T=\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk)\}$

Atom	ϱ_o	ϱ_c	$-\varrho_o''$	$-\varrho_c''$	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ca(1)	66·9	67·7	946	959	141	497	350	−30	−98	−122
Ca(2)	51·5	52·2	658	666	330	508	468	0	130	0
V(1*a*)	92·3	92·1	1380	1382	139	304	275	0	−117	0
V(1*b*)	92·6	92·4	1384	1386	139	304	275	0	−117	0
V(2)	74·3	74·6	1025	1034	159	818	288	329	−73	−292
V(3)	74·1	74·3	1022	1031	159	818	288	−329	−73	292
V(4)	91·4	92·6	1365	1388	93	506	216	−50	−75	−37
V(5)	92·9	93·4	1389	1400	92	442	210	202	−77	−39
O(1)	24·3	24·4	352	362	104	384	246	−25	−38	167
O(2)	21·1	21·0	285	289	188	538	324	182	−60	−101
O(3)	21·0	21·0	282	286	188	538	324	−182	−60	101
O(4)	20·8	20·8	261	262	164	552	219	78	−78	−23
O(5)	20·8	20·8	263	263	164	552	219	−78	−78	23
O(6)	19·0	19·2	241	244	120	1398	260	−359	10	424
O(7)	14·8	14·9	175	179	268	1156	552	449	−111	−490
O(8)	14·9	14·9	174	177	268	1156	552	−449	−111	490
O(9)	18·1	18·1	212	214	137	812	281	109	−74	−150
O(10)	18·6	18·7	219	221	137	812	281	−109	−74	150
O(11)	22·8	23·0	308	314	118	328	282	6	−49	−5
O(12)	22·5	22·8	304	311	118	328	282	−6	−49	5
O(13)	19·9	19·7	245	242	137	581	371	189	−134	−216
O(14)	20·1	19·9	260	257	146	577	350	−249	−98	185
O(15)	15·0	15·0	169	169	367	704	602	−78	−39	−299
O(16)	14·8	14·8	160	163	367	704	602	78	−39	299
O(17)	14·0	14·2	164	165	272	625	731	−442	127	−169
O(18)	11·5	11·6	110	114	315	990	807	456	45	242
O(19)	12·0	11·9	113	113	458	753	1509	522	−1126	−168
O(20)	11·7	11·8	124	124	318	1453	1262	−1049	300	63
O(21)	11·1	11·4	121	119	469	835	1101	−705	−677	297
O(22)	12·3	12·2	126	128	466	1209	703	−84	325	8
O(23)	11·8	11·9	137	138	1162	678	198	0	−496	0

Table 3. *Agreement summary*

1984 observed reflections ($12·8 \le |F_o| \le 491·0$)
$R=0·050$

Category	Limits	Number
1	$\|\Delta F\| \le 1·0\|F_{th}\|$, or $\|\Delta F\|/\|F_o\| \le 0·10$	1975
2	$1·0\|F_{th}\| < \|\Delta F\| \le 2·0\|F_{th}\|$, or $0·10 < \|\Delta F\|/\|F_o\| \le 0·15$	9

2254 unobserved reflections ($|F_c|_{max}=34·0$)

1	$\|F_c\| \le 1·0\|F_{th}\|$	2178
2	$1·0\|F_{th}\| < \|F_c\| \le 1·5\|F_{th}\|$	72
3	$1·5\|F_{th}\| < \|F_c\| \le 2·0\|F_{th}\|$	3
4	$2·0\|F_{th}\| < \|F_c\| \le 3·0\|F_{th}\|$	1

$|F_{th}|$ = threshold amplitude = 11·0 to 30·2

O(13), O(14), and Ca(1). Atoms in the body-centered positions $(\frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}+z;\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ are represented in Fig. 1 by the circles with thinner lines. Whenever it is necessary to refer to specific atoms in these sites they are distinguished by the addition of two primes and three primes, respectively, to the numbers of the atoms concerned [*e.g.* O(4''), O(4''')]. In Fig. 1 it appears that the body-centring is the result of a balance among the Coulombic attractions and repulsions of the relatively large number of electropositive and electronegative atoms in the unit cell aided by hydrogen bonds (indicated by the broken lines) to be discussed later.

The decavanadate group has orthorhombic *mmm* symmetry within the accuracy of the present measurements. This symmetry is virtually maintained even with the inclusion of Ca(1) and Ca(1') but is not retained by the whole complex ion $[(Ca\,.\,5H_2O)_2V_{10}O_{28}]^{2-}$ because of the displacement of three of the water molecules, O(17), O(18), O(19), which presumably is the result of the influence of neighbouring atoms and of the hydrogen bonding. The vanadium atoms form a condensed system of two distorted octahedra with coplanar equatorial planes and the shared edge, V(1*a*)–V(1*b*), as illustrated in Fig. 2, where the V–V distances are recorded. Each vanadium atom is coordinated with six oxygen atoms to make up the decavanadate group which consists of ten VO_6 octahedra sharing edges (Evans, Swallow & Barnes, 1964). The octahedra around V(1*a*) and V(1*b*) each share seven O–O edges with adjacent octahedra, those around V(2), V(2') and V(3), V(3') each share four edges, and those around V(4), V(4') and V(5), V(5') each share five. The interatomic distances in these octahedra are collected in Table 4. The shared O–O edges, 2·454 to 2·739 Å, are on the average appreciably shorter than the unshared edges, 2·612 to 2·803 Å. In all cases the V atoms are displaced away from the shared edges resulting in the two short V–O distances (1·681 Å) in the octahedra around V(1*a*) and V(1*b*), and the single short V–O distance (1·593 to 1·623 Å) in each of the other eight octahedra. These observations are in harmony with those reported for the VO_5 trigonal bipyramids which share edges in V_2O_5 and in certain other types of penta-

valent vanadium compounds (Bachmann & Barnes, 1961; Ahmed & Barnes, 1963*b*). The O–V–O angles vary between 74·4 and 106·8° when both oxygen atoms are on the same side as the vanadium atom, and between 153·5 and 173·2° when they are on opposite sides of V. Averaging the V–O bond lengths to conform to exact *mmm* symmetry for the decavanadate group gives the results shown in Fig. 3.

Each of the atoms Ca(1) and Ca(1′) is coordinated with two oxygen atoms of the decavanadate group, O(13) and O(14) in the first case and O(13′) and O(14′) in the second (Fig. 1), and with five water molecules,

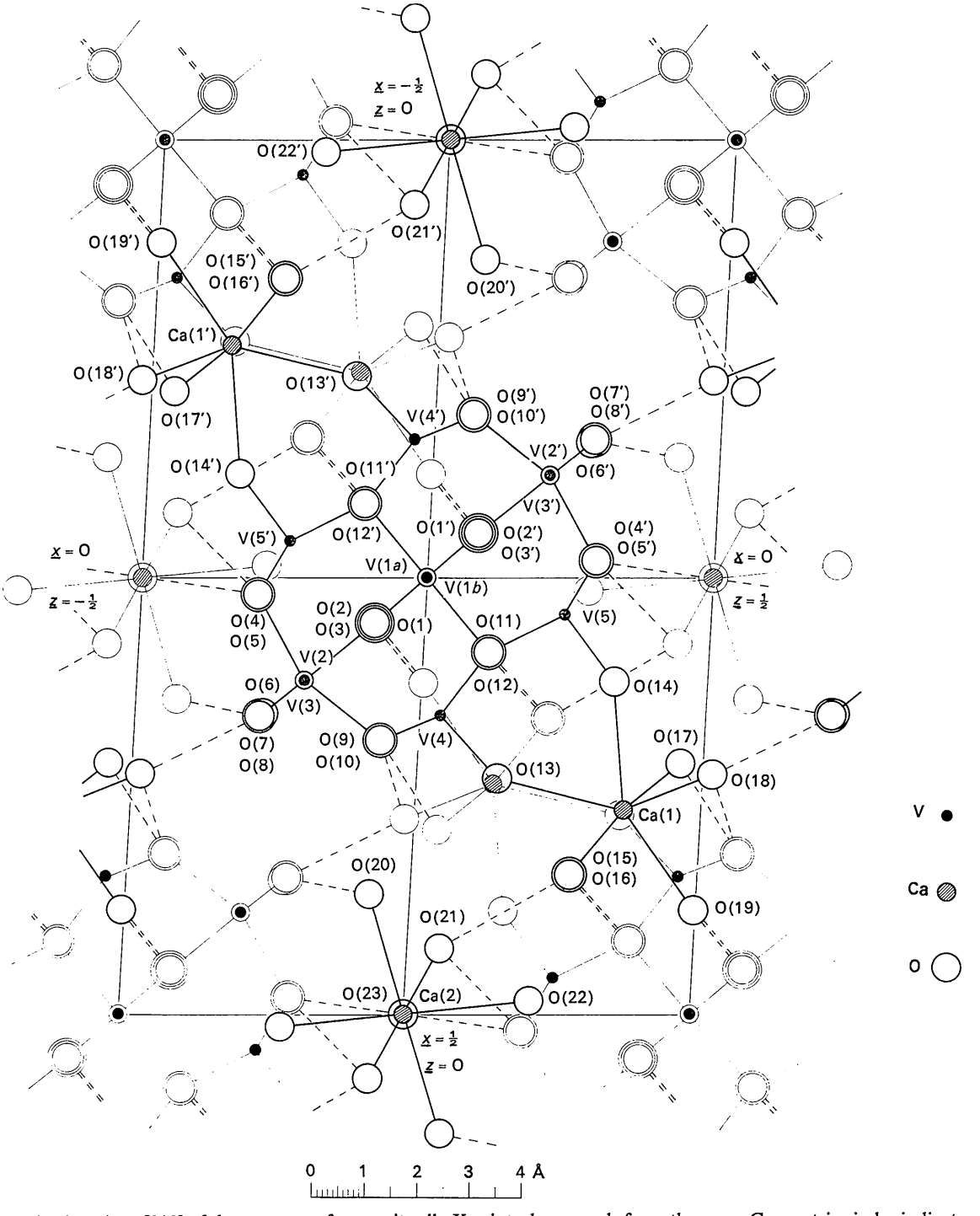

Fig. 1. Projection along [010] of the contents of one unit cell; *Y* points downwards from the page. Concentric circles indicate overlapping atoms. Broken lines indicate probable H bonds (shown as parallel where overlapping).

O(15) to O(19) around Ca(1) and their symmetrical equivalents around Ca(1′). The resulting sevenfold coordination may be considered to arise from a distorted octahedron, in which that around Ca(1), for example, has its equatorial plane defined by O(15), O(16), O(18), O(17), and has one apex at O(19), while the opposite apex has been split into two points occupied by O(13) and O(14). The separate $[Ca(H_2O)_7]^{2+}$ ion involving Ca(2) is very similar. In this case the water molecules represented by O(20), O(22), O(20′)*, O(22′)* define the equatorial plane, the single apex is at the water molecule represented by O(23) and the split apex is occupied by the water molecules represented by O(21) and O(21′)*, where the asterisks denote atoms at $1-x,y,\bar{z}$ (Fig. 1). The interatomic distances in the CaO_7 polyhedra are collected in Table 4. The Ca–O bonds vary between 2·349 and 2·459 Å with a mean of 2·407 Å, which is virtually the same as the sum of the Goldschmidt radii (2·40 Å; Megaw, 1952). The Ca(1)–V(4) and Ca(1)–V(5) distances are 3·908 and 3·917 Å, respectively.

Hydrogen bonds

Although the location of the hydrogen atoms of the water molecules could not be determined with any

Table 4. *Interatomic distances* (Å) *in the* VO_6 *and* CaO_7 *polyhedra* (*e.s.d.'s* $\times 10^3$ Å *in parentheses*)

Italics identify shared edges, square brackets designate diagonals; for V(1*a*) and V(2) read top rows and left-hand columns; for V(1*b*) and V(3) read bottom rows and right-hand columns.

	V(1*a*)	O(2)	O(2′)	O(11)	O(11′)	O(1)	
O(2)	1·681 (3)						O(3)
O(2′)	1·681 (3)	2·699 (5)					O(3′)
O(11)	1·903 (3)	2·700 (4)	2·709 (4)				O(12)
O(11′)	1·903 (3)	2·709 (4)	2·700 (4)	[3·705 (4)]			O(12′)
O(1)	2·135 (3)	*2·662 (4)*	[3·785 (4)]	*2·592 (4)*	*2·599 (4)*		O(1)
O(1′)	2·135 (3)	[3·785 (4)]	*2·662 (4)*	*2·599 (4)*	*2·592 (4)*	*2·683 (4)*	O(1′)
	V(1*b*)	O(3)	O(3′)	O(12)	O(12′)	O(1)	
	V(2)	O(7)	O(6)	O(9)	O(4)	O(2)	
O(7)	1·593 (5)						O(8)
O(6)	1·818 (4)	2·704 (7)					O(6)
O(9)	1·867 (4)	2·710 (7)	2·660 (6)				O(10)
O(4)	1·874 (4)	2·691 (6)	2·647 (5)	[3·641 (5)]			O(5)
O(2)	2·077 (3)	2·803 (6)	[3·814 (5)]	2·612 (5)	2·627 (5)		O(3)
O(1)	2·313 (3)	[3·900 (6)]	*2·739 (5)*	*2·632 (5)*	*2·639 (4)*	*2·662 (4)*	O(1)
	V(3)	O(8)	O(6)	O(10)	O(5)	O(3)	
	V(4)	O(13)	O(9)	O(10)	O(11)	O(12)	
O(13)	1·623 (3)						
O(9)	1·813 (4)	2·722 (6)					
O(10)	1·813 (4)	2·722 (6)	2·689 (6)				
O(11)	2·002 (3)	2·737 (5)	2·697 (5)	[3·725 (5)]			
O(12)	2·002 (3)	2·737 (5)	[3·725 (5)]	2·697 (5)	*2·454 (4)*		
O(1)	2·211 (3)	[3·824 (4)]	*2·632 (5)*	*2·632 (5)*	*2·592 (4)*	*2·592 (4)*	
	V(5)	O(14)	O(4′)	O(5′)	O(11)	O(12)	
O(14)	1·617 (3)						
O(4′)	1·803 (4)	2·709 (5)					
O(5′)	1·803 (4)	2·709 (5)	2·681 (5)				
O(11)	2·009 (3)	2·735 (5)	2·696 (5)	[3·721 (5)]			
O(12)	2·009 (3)	2·735 (5)	[3·721 (5)]	2·696 (5)	*2·454 (4)*		
O(1′)	2·222 (3)	[3·828 (4)]	*2·639 (4)*	*2·639 (4)*	*2·599 (4)*	*2·599 (4)*	
	Ca(1)	O(19)	O(15)	O(16)	O(18)	O(17)	O(13)
O(19)	2·383 (9)						
O(15)	2·383 (6)	3·025 (10)					
O(16)	2·383 (6)	3·045 (10)	3·510 (7)				
O(18)	2·363 (8)	3·043 (11)	[4·649 (10)]	3·347 (11)			
O(17)	2·429 (6)	3·453 (10)	3·026 (9)	[4·792 (8)]	3·507 (10)		
O(13)	2·442 (3)	[4·518 (10)]	2·886 (7)	2·886 (7)	[4·343 (9)]	[4·014 (7)]	
O(14)	2·459 (3)	[4·661 (9)]	[4·191 (8)]	[4·191 (8)]	2·976 (9)	2·819 (7)	2·895 (5)
	Ca(2)	O(23)	O(20)	O(22)	O(20′)*	O(22′)*	O(21)
O(23)	2·349 (6)						
O(20)	2·414 (7)	3·214 (14)					
O(22)	2·412 (6)	3·125 (9)	3·690 (9)				
O(20′)*	2·414 (7)	3·214 (14)	[4·809 (9)]	3·064 (10)			
O(22′)*	2·412 (6)	3·125 (9)	3·064 (10)	[4·777 (8)]	3·690 (9)		
O(21)	2·429 (7)	[4·539 (10)]	2·763 (11)	3·027 (11)	[4·185 (11)]	[4·107 (11)]	
O(21′)*	2·429 (7)	[4·539 (10)]	[4·185 (11)]	[4·107 (11)]	2·763 (11)	3·027 (11)	2·886 (12)

certainty from the final difference maps, it is obvious from the structure (Fig. 1) that the oxygen atoms O(15) to O(22) inclusive, and their symmetrical equivalents O(15′) to O(22′) inclusive, together with O(23), represent the $17H_2O$ per formula unit of pascoite. Arbitrarily selecting 3·15 Å as the longest O–O distance reported as a hydrogen bond in inorganic salts (Pimentel & McClellan, 1960), the shortest H_2O–O distances in the present structure are listed in Table 5. The configurations of nearest neighbours around eight of the nine non-equivalent water molecules are represented in Fig. 4. The water molecule designated by O(22) has been omitted because it approaches only one oxygen atom, O(16), also a water molecule, at the rather long distance of 2·999 Å within the adopted minimum; the angle Ca(2)–O(22)–O(16) is 113·8°, and the next closest oxygen atom is O(2″)* of the decavanadate group at 3·199 Å from O(22) with the angles O(16)–O(22)–O(2″)* = 76·4° and Ca(2)–O(22)–O(2″)* = 133·9°.

From Fig. 4 and Table 5 it seems possible that all O–O distances involving one of the water molecules, and less than 2·9 Å in length, may represent O–H···O bonds, with the possibility that one or two of the longer distances might also be included. In six cases, O(15), O(18), O(19), O(20), O(21), O(23), the water molecules are associated with Ca–O–O triangles in each of which the two H_2O–O distances suggest hydrogen bonds (Fig. 4). The perpendicular distances of the water molecules from the planes of their associated triangles are 0·23 Å for O(15), 0·10 Å for O(18) and for O(19), 0·99 Å for O(20), and 1·12 Å for O(21); O(23) is coplanar with Ca(2), O(4″)*, and O(4‴)*. The small (74·0°) angle O(8)*–O(18)–O(9‴)* may be an indication that the protons are outside the lines O(18)–O(8)* and O(18)–O(9‴)*, and this may also be the case in the triangle around O(21). The relatively long distance of O(20) from the plane Ca(2)–O(8‴)*–O(7‴)* suggests that O(20)–O(8‴)* may not involve a hydrogen bond, particularly in view of the interatomic distance (2·963 Å) concerned, and the still greater distance of O(21) from the plane Ca(2)–O(5″)–O(15) may be the result of its environment and the fact that O(15) also appears to be hydrogen bonded to O(12‴). Values of the following angles have been omitted from Fig. 4 for simplification of the diagrams: Ca(1)–O(16)–O(22) = 99·4°, O(11‴)*–O(16)–O(22) = 96·9°, O(22)–O(16)–O(17‴)* = 104·9°; Ca(1)–O(17)–O(7)* = 136·5°, O(10‴)–O(17)–O(7)* = 70·3°, O(16‴)–O(17)–O(7)* = 125·6°; Ca(1)–O(18)–O(21‴)* = 113·5°, Ca(1)–O(18)–O(6)* = 111·6°, O(9‴)*–O(18)–O(21‴)* = 94·4°, O(9‴)*–O(18)–O(6)* = 118·5°, O(8)*–O(18)–O(21‴)* = 67·5°, O(8)*–O(18)–O(6)* =

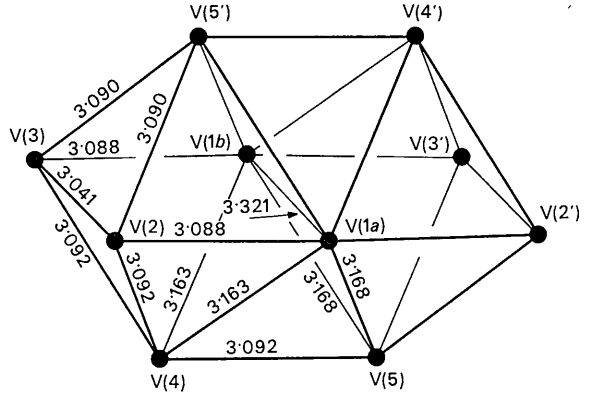

Fig. 2. Perspective view of the V atoms in the decavanadate group; V–V distances in Å.

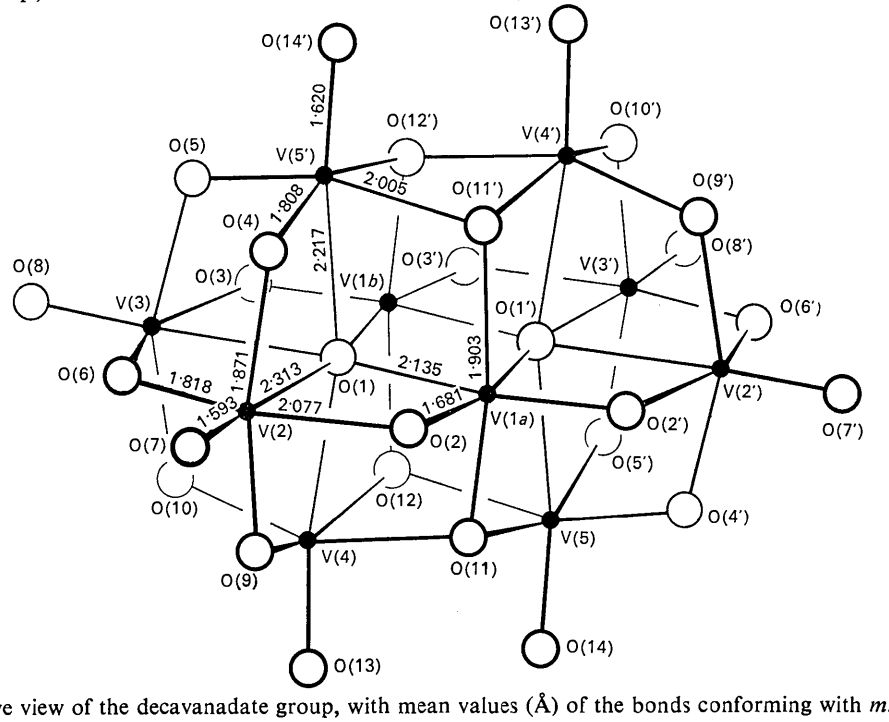

Fig. 3. Perspective view of the decavanadate group, with mean values (Å) of the bonds conforming with *mmm* symmetry.

54·7°, O(21‴)*–O(18)–O(6)* = 94·9°; Ca(2)–O(21)–O(18‴) = 141·6°, O(18‴)–O(21)–O(15) = 79·9°, O(18‴)–O(21)–O(5″) = 107·1°.

The more probable hydrogen bonds are indicated with broken lines in Fig. 1 and are shown as closely spaced parallel lines when they overlap in the projection. Examination of Figs. 1 & 4 and Table 5 (with special attention to the atomic coordinates designated by the primes and asterisks – see heading of Table 5) indicates that H bonds provide weak links throughout the structure among the hydrated complex Ca(1)-decavanadate ions themselves, and among these and the hydrated Ca(2) ions.

Slow crystallization from water by simple evaporation over a period of about two months yields well-

Table 5. *Distances less than* 3·15 Å *between the* H_2O *molecules (at x, y, z) and the nearest* O *or* OH_2

Single, double, and triple primes designate atoms at $\bar{x}$, y, $\bar{z}$; $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{2}+z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$, respectively; an asterisk indicates a translation of -1 along y and/or ± 1 along z.

Atoms	l	Atoms	l
O(17)–O(10‴)	2·681 Å	O(19)–O(2‴)*	2·846 Å
O(16)–O(11‴)*	2·694	O(18)–O(8)*	2·846
O(15)–O(12‴)	2·694	O(21)–O(15)	2·863
O(23)–O(4″)*	2·702	O(20)–O(8‴)*	2·963
O(23)–O(4‴)*	2·702	O(17)–O(16‴)	2·996
O(18)–O(9‴)*	2·741	O(22)–O(16)	2·999
O(21)–O(5″)	2·774	O(18)–O(21‴)*	3·023
O(20)–O(7‴)*	2·790	O(18)–O(6)*	3·029
O(19)–O(3‴)	2·817	O(17)–O(7)*	3·128

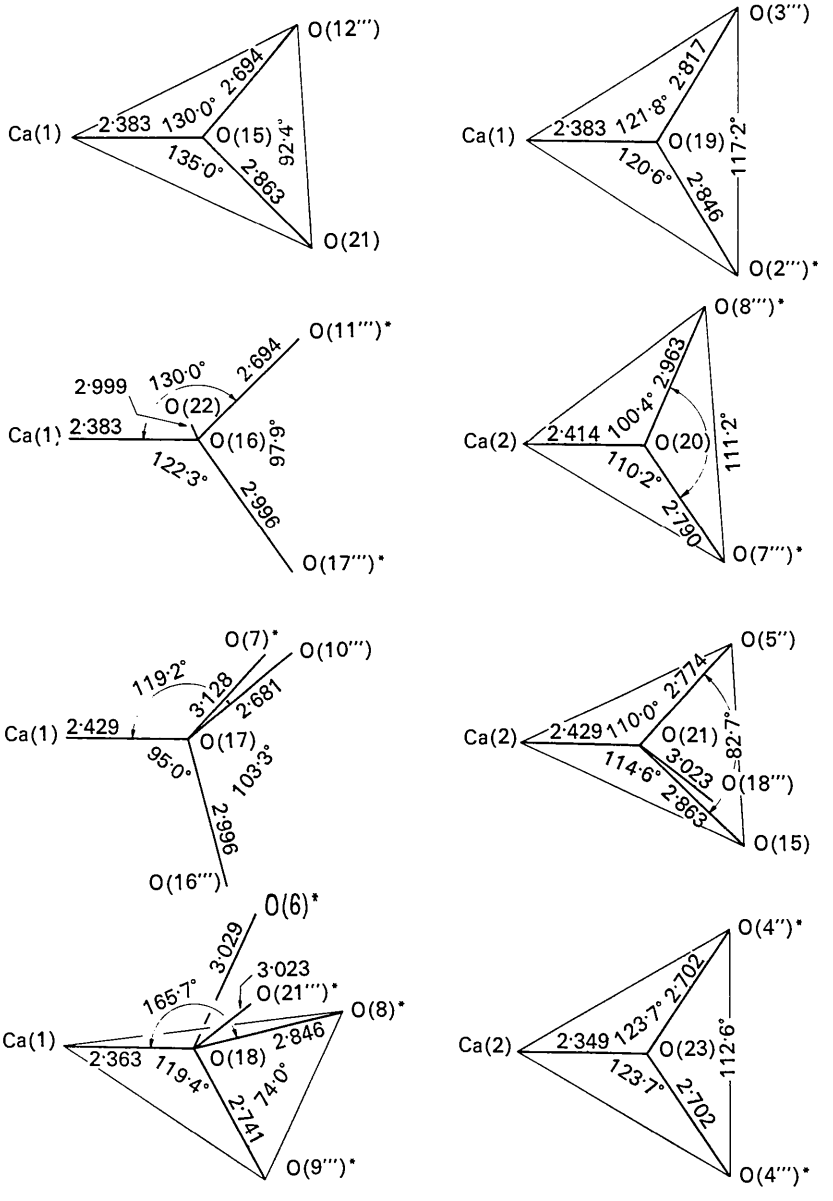

Fig. 4. Nearest neighbours less than 3·15 Å from 8 of the 9 non-equivalent H_2O molecules (interatomic distances in Å).

formed single crystals of pascoite with dimensions of at least $1 \times 0{\cdot}5 \times 0{\cdot}5$ mm. It is probable that the size could be increased to one more advantageous for a neutron diffraction investigation, and there should be no difficulty in preparing deuterated pascoite with optimum H_2O/D_2O ratio. With so many water molecules involved it would be of great interest to determine if the sites of the protons could be established unequivocally by neutron diffraction methods.

We are indebted to Professor Clifford Frondel, Harvard University, for some of the original type material of Hillebrand, Mervin & Wright (1914), and for part of the specimen examined by Berman (Palache, Berman & Frondel, 1951, p. 1055), and to Mr D. M. Hausen, Union Carbide Nuclear Company, Colorado, for a sample of particularly fine crystals of synthetic pascoite prepared by Mr J. Lane. Also available have been specimens synthesized by Dr H. G. Bachmann (N.R.C. Postdoctorate Fellow, 1956–58) in this laboratory in addition to those prepared during the present investigation. Grateful acknowledgement is made to Dr H. T. Evans, Jr. for powder patterns of natural and synthetic pascoite specimens at the U.S. Geological Survey for comparison with those in this laboratory, for making available his final results on the structure of $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ prior to publication, and for permission to make use of his perspective drawing of the decavanadate ion on which the present Figs. 2 & 3 are based. A preliminary examination of the [010] projection of pascoite was carried out by Dr H. G. Bachmann in 1961–62 at Göttingen, through the courtesy of Professor J. Zemann, and we are grateful to Dr Bachmann for turning over his data to us when he joined an industrial research laboratory in 1963.

All computations for the present investigation were carried out on an IBM 1620 computer with programs written by Ahmed, Gabe, Mair & Pippy (1963), and the valuable assistance of Mrs M. E. Pippy in the computational work is greatly appreciated.

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