Discussion. The Au atom lies 0·020 (2) Å from the plane of the four Cl atoms; since this is about one tenth of the r.m.s. thermal amplitude of the Au atom normal to the plane, for chemical purposes the ion may be considered to possess $4/mmm$ symmetry. The Au–Cl distance of 2·271 Å is consistent with previous measurements [*e.g.* 2·273 Å in ammonium tetrachloroaurate(III): Bonamico, Dessy, Furlani & Capece (1973)]. The cation has crystallographic $\bar{4}$ symmetry; the C–As bond is tilted by 4·1° with respect to the plane of the phenyl group, and the smallest dihedral angles about the C–As bond are: C(6)–C(1)–As–C(1)^v $-15\cdot1°$, C(2)–C(1)–As–C(1)^{iii} 39·0°, C(2)–C(1)–As–C(1)^{iv} $-82\cdot1°$ and C(6)–C(1)–As–C(1)^{iv} 102·6°.* There are no short interionic contacts, which simplifies the interpretation of the Mössbauer spectra.

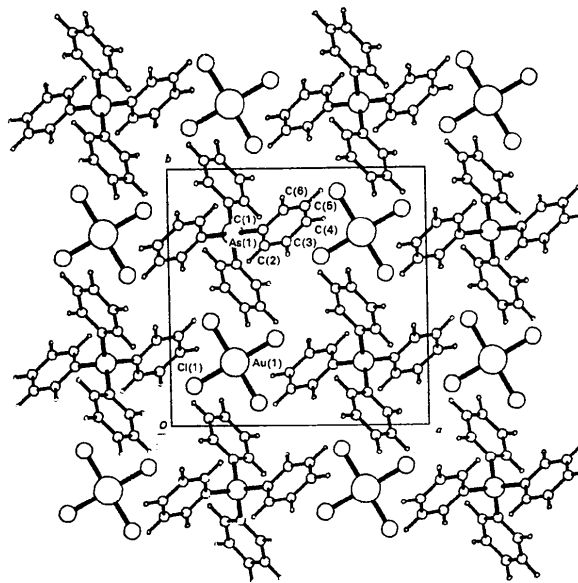* For symmetry transformations see Table 2.

Fig. 1. The structure in projection down **c**.

Reference

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Calcium Divanadate Dihydrate

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Abstract. $Ca_2V_2O_7.2H_2O$, triclinic, $P\bar{1}$, $a = 8\cdot1344$ (6), $b = 8\cdot2019$ (7), $c = 6\cdot8683$ (5) Å, $\alpha = 96\cdot238$ (7)°, $\beta = 113\cdot355$ (6)°, $\gamma = 106\cdot192$ (8)°, $Z = 2$, $D_x = 2\cdot801$, $D_m = 2\cdot81$ (2) g cm^{-3}. Anisotropic refinement of 1730 Mo $K\alpha$ counter-measured data to $R = 0\cdot070$. The structure contains layers of packed $V_2O_7^{4-}$ groups and H_2O molecules, interleaved with Ca^{2+} ions.

Introduction. In a study of the chemistry of calcium vanadates in aqueous solution, Marvin & Magin (1959) obtained two crystalline products in the region of pH 8–9, which by analysis proved to be $Ca_2V_2O_7.2H_2O$ and $Ca_2V_2O_7$. We have carried out a crystal-structure determination of crystals from Marvin & Magin's original sample of the dihydrate, and the results are reported here. The crystals were prepared from a stock solution 0·04 M in CaO and 0·08 M in V_2O_5, having a pH of about 5, which was adjusted to about pH 8 by adding a solution of $Ca(OH)_2$, filtered and then evaporated at room temperature. A static thermogravi-metric experiment (samples heated to various temperatures for 24 h, then cooled and weighed) showed that the dihydrate is converted to a monohydrate at 130 °C and to the anhydrous state at 220 °C ($\pm$ 10°).

Schwendt, Petrovič & Žúrková (1971), in a study of solid alkaline earth divanadates, formed three compounds $Ca_2V_2O_7.2H_2O$, $Ca_2V_2O_7.H_2O$ and $Ca_2V_2O_7$. As far as we can tell from the meagre X-ray powder data of Schwendt *et al.* as compared with ours, our dihydrate and anhydrous phases are identical with their corresponding ones. They reported the results of DTA, TGA, and IR studies but gave no crystallographic information. According to Pedregosa, Baran & Aymonino (1973), $Ca_2V_2O_7$ is isostructural with tetragonal β-$Sr_2V_2O_7$.

$Ca_2V_2O_7.2H_2O$ forms colorless, lath-like, parallelogram-shaped crystals, bounded laterally by $\{1\bar{1}1\}$ and $\{2\bar{1}\bar{1}\}$ and flattened parallel to (100) (angle on face = 79·4°). The crystal used for intensity measurements was 0·15 × 0·15 × 0·015 mm in size, and was considered

to be small enough and of low enough density to allow absorption corrections to be neglected ($\mu = 34\cdot2$ cm^{-1}). The unit-cell parameters were refined by least-squares analysis of X-ray powder data measured from a Guinier–Hägg pattern made with Cr $K\alpha_1$ radiation ($\lambda = 2\cdot28962$ Å). (These data have been submitted to the Joint Committee on Powder Diffraction Standards.) With the Picker automatic diffractometer, 2482 reflec-

tions were measured in the hemisphere bounded by the limit (sin $\theta)/\lambda = 0\cdot7$, using Mo $K\alpha$ radiation. Of these, 1730 independent reflections, whose observed F values were greater than 3σ according to counting statistics, were used for the structure analysis and refinement. These data were normalized to E values and treated with the symbolic addition procedure for sign determination (Karle & Karle, 1966) using the programs con-

Table 1. *Structural and thermal parameters for* Ca$_2$V$_2$O$_7$.2H$_2$O

The thermal function is $T = \exp[-(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)/4]$.

|	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cations (U_{ij} as above $\times 10^4$)									
Ca(1)	0·0766 (3)	0·6901 (3)	0·8836 (3)	48 (7)	75 (7)	90 (7)	−3 (6)	26 (6)	4 (6)
Ca(2)	0·0984 (3)	0·2277 (3)	0·6855 (3)	60 (8)	87 (7)	116 (8)	28 (6)	49 (6)	40 (6)
Divanadate group ($U_{ij} \times 10^4$ for V, $\times 10^3$ for O)									
V(1)	0·2642 (2)	0·1314 (2)	0·2626 (2)	3 (8)	64 (6)	58 (6)	−2 (5)	2 (5)	7 (5)
V(2)	0·7406 (2)	0·3550 (2)	0·5190 (2)	10 (7)	50 (6)	51 (6)	−11 (5)	10 (5)	4 (5)
O(1)	0·4970 (10)	0·2620 (10)	0·4788 (11)	5 (3)	22 (4)	11 (3)	0 (3)	3 (3)	−1 (3)
O(2)	0·1788 (9)	0·2490 (9)	0·0809 (11)	7 (3)	16 (3)	12 (3)	6 (3)	4 (3)	4 (3)
O(3)	0·2841 (9)	−0·0354 (9)	0·1219 (11)	6 (3)	15 (3)	12 (3)	1 (3)	3 (3)	2 (3)
O(4)	0·1044 (9)	0·0602 (9)	0·3634 (12)	4 (3)	15 (3)	13 (3)	−5 (2)	6 (3)	−4 (3)
O(5)	0·7935 (10)	0·2320 (9)	0·3568 (11)	11 (3)	10 (3)	14 (3)	1 (3)	8 (3)	1 (3)
O(6)	0·7968 (10)	0·5605 (9)	0·4902 (12)	10 (3)	13 (3)	14 (3)	1 (3)	4 (3)	3 (3)
O(7)	0·9049 (8)	0·3745 (8)	0·7781 (10)	2 (3)	11 (3)	5 (3)	−2 (2)	−2 (2)	1 (2)
H$_2$O molecules ($U_{ij} \times 10^3$)									
O(8)	0·6863 (10)	0·4585 (10)	0·0216 (13)	8 (3)	19 (4)	22 (4)	3 (3)	7 (3)	8 (3)
O(9)	0·6194 (10)	0·8504 (10)	0·1597 (12)	11 (3)	22 (4)	17 (4)	9 (3)	6 (3)	5 (3)
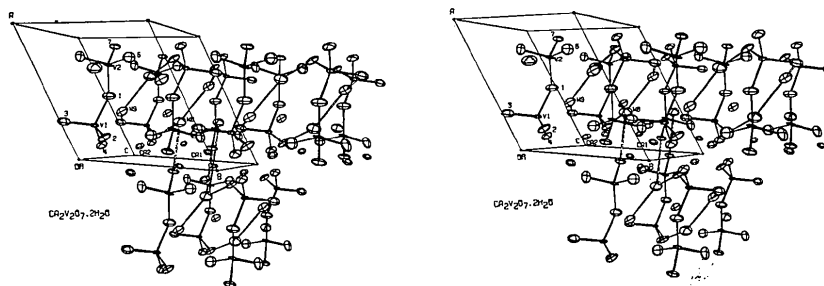
Fig. 1. General stereoscopic view of the structure of Ca$_2$V$_2$O$_7$.2H$_2$O, looking edgewise at the anion–water layers. Large ellipsoids (corresponding to 50% probability) are water molecules with hydrogen bonds to neighboring atoms indicated by open links. Small unattached ellipsoids are Ca^{2+} ions.
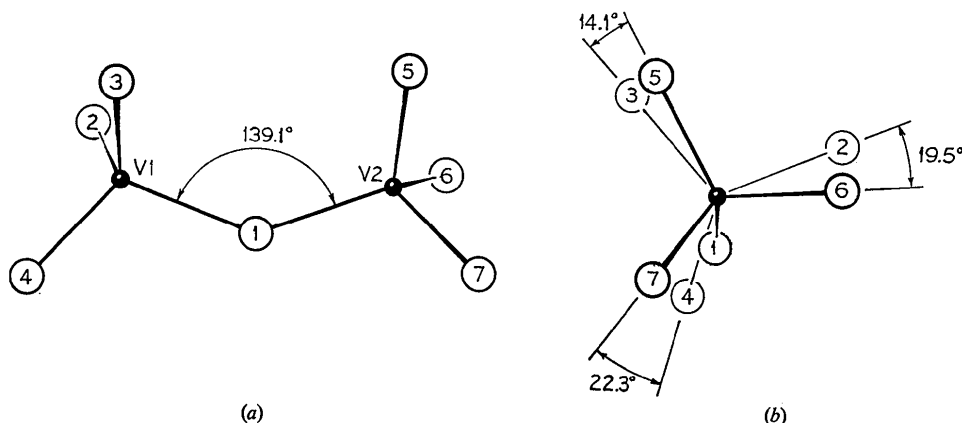

(a) (b)

Fig. 2. Orthographic side view (a) and end view along the V–V vector (b) of the V$_2$O$_7^{4-}$ anionic group.

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tained in the system X-RAY67 written by Professor J. M. Stewart of the University of Maryland. The strongest sign indications still left a fourfold ambiguity, which required the interpretation of the corresponding Fourier syntheses. Judging by the number of large peaks in these maps and their reasonable crystal chemical meaning, the correct phase set was selected and verified by a series of electron density–structure factor cycles until all atoms were clearly resolved. The resulting structure was passed through 11 cycles of full-matrix least-squares analysis based on $F(obs)$ data with equal unit weights (using the *RFINE* program of Dr L. Finger of the Geophysical Laboratory), converging in full anisotropic mode to $R = 0.070$. Dispersion corrections (but none for absorption or extinction) were included in the last cycles. The resulting parameters are given in Table 1. All the thermal motions are rather low, and in the last stage, V(1) and O(7) had ellipsoid parameters that were nonpositive definite but not significantly so. One standard deviation unit has been added to U_{11} for these atoms to obtain the values shown in Table 1, in order to make them real.*

Discussion. The general class of compounds $X_2Y_2O_7$, according to Brown & Calvo (1970), can be classified into a small number of structurally related groups. The largest of these, which they call the 'dichromate' group, is based on structures in which the Y_2O_7 groups are packed side by side into extended layers, with their long axes roughly normal to the layer. The cations are found between the layers, holding them together. $Ca_2V_2O_7.2H_2O$ belongs to this group, having a one-layer structural unit in which the layer has been expanded to enclose the water molecules. Fig. 1 shows a general view of the structure looking into the edge of these sheets.

The $V_2O_7^{4-}$ group, illustrated in Fig. 2(*a*), has a bent, approximately eclipsed configuration, which is generally characteristic of this group of structures. Fig. 2(*b*) shows the molecule viewed along the V–V axis, so that the deviation from exact eclipsing of the two tetrahedra, corresponding to a twist of about 18°, can be seen. As expected, the V–O bond to the linking O(1) (avg. 1.80 Å) is considerably longer than the terminal bonds (avg. 1.69 Å), and this link is strongly bent ($139.1 \pm 1.1°$). The individual dimensions are shown in Table 2. The average dimensions are quite analogous to those found in tetragonal β-$Sr_2V_2O_7$ by Baglio & Dann (1972), who also reviewed data published for other divanadates ($Pb_2V_2O_7$, $Mn_2V_2O_7$, $Cd_2V_2O_7$). For

the strontium compound, they report average V–O bond lengths of 1.81 Å for the linking oxygen atom and 1.70 Å for the unlinked atoms (individual distances determined to ± 0.03 Å).

Table 2. *Interatomic distances in* $Ca_2V_2O_7.2H_2O$ (Å)

Divanadate group		Cation coordination (< 3.0 Å)	
V(1)–O(1)	1.798 (7)	Ca(1)–O(2)	2.359 (7)
–O(2)	1.708	–O(3)	2.341
–O(3)	1.672	–O(5)	2.340
–O(4)	1.697	–O(6)	2.601
V(2)–O(1)	1.804	–O(7)	2.392
–O(5)	1.678	–O(7')	2.439
–O(6)	1.674	–O(8)	2.472
–O(7)	1.707	Ca(2)–O(2)	2.500
		–O(4)	2.371
Probable hydrogen bonds		–O(4')	2.497
(< 2.9 Å)		–O(5)	2.623
O(8)–O(2)	2.638 (10)	–O(6)	2.375
–O(7)	2.871	–O(7)	2.451
O(9)–O(3)	2.797	–O(8)	2.704
–O(8)	2.737	–O(9)	2.416

The Ca^{2+} ions are both coordinated with oxygen atoms in a configuration that may be approximately described as trigonal prismatic, and one vertical prism edge [O(7)–O(8)] is shared between Ca(1) and Ca(2). Ca(1) is 7-coordinated with an additional O atom in the center of one prism face, and its average Ca–O bond length is 2.42 Å, ranging from 2.34 to 2.60 Å (including all < 3.0 Å). Ca(2) is 8-coordinated, with O atoms centered on two prism faces, and its average bond length is 2.49 Å, ranging from 2.37 to 2.70 Å. The nearest Ca–Ca approach is 3.80 Å.

The H_2O molecules have distances to neighboring oxygen atoms that suggest well developed hydrogen bonds. A plausible interpretation of the bond lengths suggests that $H_2O(8)$ has hydrogen atoms directed toward O(2) (2.64 Å) and O(7) (2.87 Å), and $H_2O(9)$ has hydrogen atoms associated with O(3) (2.80 Å) and $H_2O(8)$ (2.74 Å). One of the bonds [$H_2O(8)$ to O(7)] bridges the interlayer region. These links are indicated in Fig. 1.

The details of interatomic distances are given in Table 2.

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31154 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.