the zeolitic nature of the water molecules. The Jahn–Teller effect is observed in the Cu octahedron. The As atom exhibits the usual tetrahedral coordination by O atoms. The *M* atom shows (6 + 3) coordination by the O atoms in the form of a tricapped trigonal prism. The trigonal planes are perpendicular to the *c* axis.

The H atoms could not be located in the difference Fourier maps. To distinguish O^{2-}, OH^-, and H_2O in the oxygen positions, the bond-valence sums were calculated following the method of Donnay & Allmann (1970) using the values of the bond lengths and coordination numbers. This method is based on Pauling's (1929) principle of local neutralization of charge. The ideal values of the bond-valence sums are 2, 1, and 0 for O^{2-}, OH^-, and H_2O, respectively. The bond-valence sums $\sum c_v$, listed in Table 1, clearly show that O(1) and O(2) are oxygen ions, while O(4) and O(5) correspond to the hydroxyl group. In contrast the valence sum of atom O(3) is 1·78, suggesting the presence of partial substitution of oxygen ions by the hydroxyl ion in this position. Accordingly, it is found that, on substitution of Ca^{2+} for a trivalent cation, the charge compensation is accomplished by the concomitant substitution of OH^- for O^{2-} at the O(3) position.

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Tetracaesium Divanadate Dihydrate, $Cs_4V_2O_7.2H_2O$

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Abstract. $M_r = 781{\cdot}53$, monoclinic, $P2_1/c$, $a = 9{\cdot}196\,(1)$, $b = 17{\cdot}863\,(2)$, $c = 9{\cdot}059\,(1)$ Å, $\beta = 111{\cdot}81\,(1)°$, $V = 1381{\cdot}6\,(2)$ Å^3, $Z = 4$, $D_x = 3{\cdot}757$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 12{\cdot}0$ mm^{-1}, $F(000) = 1368$, $T = 298$ K. Final $R = 0{\cdot}071$ for 3417 unique observed reflections. The V_2O_7 group has a nearly staggered conformation with a V—O—V angle of 174 (1)°. The Cs^+ ions are surrounded by eight to nine O atoms of the V_2O_7 groups and the H_2O molecules.

Introduction. An unknown, highly hygroscopic phase was obtained from aqueous solution of $2Cs_2O.V_2O_5$ by evaporation at 373 K. A structure determination revealed its chemical composition to be $Cs_4V_2O_7.2H_2O$.

Experimental. Crystal of irregular rounded shape 0·15 × 0·2 × 0·3 mm, enclosed in thin-wall (0·01 mm) glass capillary. Four-circle Rigaku diffractometer, lattice constants based on 29 reflections with $29 < 2\theta < 35°$. Intensity measurement up to $(\sin\theta)/\lambda = 0{\cdot}704$ Å^{-1} within the range h ±12, k 0→25, l ±12 performed in several separate runs; frequent redetermination of the orientation matrix necessary. $2\theta/\omega$-scanning, scanning range $\Delta\omega = 1{\cdot}2° + 0{\cdot}5° \tan\theta$ and speed 2° min^{-1}. Absorption correction not practicable because of difficulties in measuring specimen shape. Intensities reduced to common scale using standard reflections $\bar{2}40$, $30\bar{2}$ and $\bar{4}00$. 8247 reflections measured, 1697 unobserved [$I < \sigma(I)$ or too weak to be scanned], 6550 considered observed, 3417 unique reflections, $R_{\rm int} = \sum|F_j - \bar{F}_j|/\sum F_j = 0{\cdot}059$. Structure

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solved by Patterson method. Atomic coordinates, anisotropic thermal parameters, a scale factor and a free parameter for extinction correction refined by least squares based on F. $R = 0{\cdot}071$, $R_w = 0{\cdot}072$, $S = 6{\cdot}76$; weight $w = 1/\sigma^2$ [$\sigma = \sigma(I)F/(2I)$]. Extinction correction according to Zachariasen (1967, 1968) using a simplified expression

$$F_c = sF[1 + (g/\sin 2\theta)\,(1 + \cos^4 2\theta \cos^4 2\theta_M) \times (1 + \cos^2 2\theta \cos^2 2\theta_M)^{-1} F^2]^{-1/4},$$

where $s = 0{\cdot}721$ (3), $g = 1{\cdot}74\,(5) \times 10^{-6}$ and $2\theta_M = 12{\cdot}17°$. $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·0002, $\Delta\rho$ $-5{\cdot}4 \sim 3{\cdot}2$ e Å^{-3}. Atomic scattering factors of Cromer & Mann (1968), dispersion corrections of Cromer & Liberman (1970). Computer programs used: *RSLC*3 in *UNICS* system (Sakurai, 1967), *ORFFE* (Busing, Martin & Levy, 1964), version 2 of *ORTEP* (Johnson, 1965), and other unpublished programs written by one of the authors.

Discussion. The positional and equivalent isotropic thermal parameters are listed in Table 1.* The O atoms not belonging to the V_2O_7 group were considered to be those of water molecules, Aq(1) and Aq(2). Fig. 1 illustrates the structure as viewed along [001]. The V—O bond lengths and the V—O—V angle are shown in Fig. 2. The V_2O_7 group has a nearly staggered conformation. Hawthorne & Calvo (1978) summarized selected data for the divanadate structure and noted a general tendency for longer average V—O(br) distances to be associated with smaller V—O(br)—V angles. Compared with V_2O_7 groups in the divalent metal divanadates cited by those authors, the V_2O_7 group in $Cs_4V_2O_7.2H_2O$ has V—O(br) bonds much longer than those expected for a large V—O(br)—V angle of 174°. This observation suggests that the V_2O_7 group in this compound is strongly distorted as a result of coordination to large Cs^+ ions and thus may be relatively unstable compared with undistorted ones, *e.g.* in aqueous solution. The highly hygroscopic nature of $Cs_4V_2O_7.2H_2O$ might perhaps be related to this distortion of the V_2O_7 group. The stretching of V—O(br) bonds is, however, compensated by short V—O(nbr) bonds to give a total average V—O bond length of 1·71 Å, a value commonly found for V_2O_7 groups with nearly straight V—O—V bridging [Fig. 3 in Kato & Takayama (1983)].

The Cs^+ ions are surrounded by eight to nine O atoms with Cs—O distances listed in Table 2. Short O—O distances implying hydrogen bonds are also given in Table 2. The bond valence s was calculated for the cation–oxygen bonds using the expression $s = (R/R_1)^{-N}$ of Brown & Wu (1976), where R represents the length of the bond (Å) and empirical constant N is 6·6 for Cs and 5·1 for V. R_1 was adjusted in such a way that the sum of the bond valences calculated becomes equal to the formal charge of each cation. The values thus obtained, 2·334 Å for Cs and 1·773 Å for V, were used for the bond-valence calculation whose results are summarized in Table 3.* The sums of bond valences of

Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Cs(1)	0·1788 (2)	0·22698 (9)	0·0066 (2)	2·47 (3)
Cs(2)	0·2677 (2)	0·00549 (8)	0·6104 (2)	1·99 (3)
Cs(3)	0·2618 (2)	−0·03204 (8)	0·1301 (2)	2·04 (3)
Cs(4)	0·7059 (1)	0·25332 (7)	0·2296 (2)	2·00 (3)
V(1)	0·0100 (4)	0·1076 (2)	0·2536 (4)	1·16 (6)
V(2)	0·4279 (4)	0·1423 (2)	0·3710 (4)	1·11 (5)
O(1)	−0·030 (2)	0·0172 (7)	0·212 (2)	2·0 (3)
O(2)	−0·045 (2)	0·1357 (9)	0·402 (2)	2·2 (3)
O(3)	−0·083 (2)	0·1585 (7)	0·094 (2)	1·7 (2)
O(4)	0·222 (2)	0·1204 (9)	0·320 (2)	3·0 (3)
O(5)	0·454 (2)	0·2343 (8)	0·383 (2)	2·2 (3)
O(6)	0·483 (2)	0·1094 (8)	0·226 (2)	2·1 (3)
O(7)	0·531 (2)	0·1015 (8)	0·543 (2)	2·2 (3)
Aq(1)	−0·022 (2)	0·3692 (9)	0·208 (2)	3·4 (4)
Aq(2)	0·447 (2)	0·3890 (9)	0·417 (2)	3·4 (4)

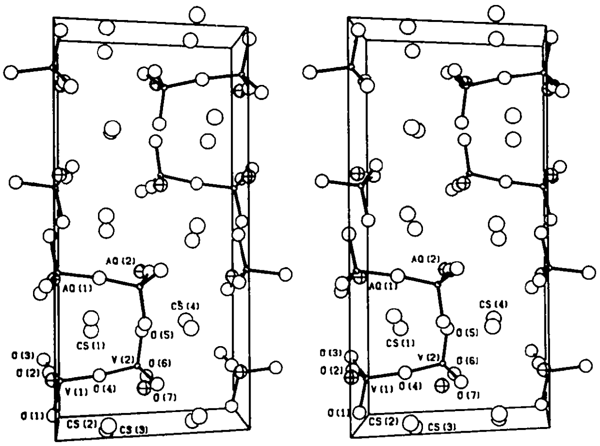

Fig. 1. Stereoscopic view of the structure along [001].

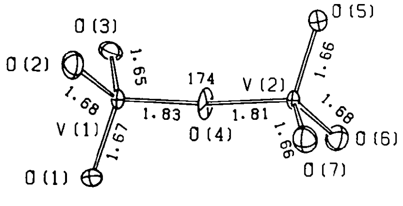

Fig. 2. V—O distances (Å) and V—O—V angle (°) in V_2O_7 group. E.s.d.'s are 0·014 ~ 0·015 Å and 1·2°.

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* Lists of structure amplitudes, anisotropic thermal parameters and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39802 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* This table has been deposited. See deposition footnote.

Aq(1) and Aq(2) (both 0·302) show that these O atoms belong to water molecules, and those of O(1), O(2), O(5) and O(6) (range 1·795–1·879) correspond to the fact that these take part in hydrogen bonds. For the other O atoms, the sum of bond valences is in the range 1·891–2·150.

Table 2. *Distances* (Å) *and angles* (°)

Symmetry code
(i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$
(ii) $1-x, -y, 1-z$
(iii) $-x, -y, 1-z$
(iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$
(v) $-x, -y, -z$
(vi) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(vii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(viii) $1+x, y, z$
(ix) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$
(x) $-x, \frac{1}{2}+y, \frac{1}{2}-z$

(*a*) Cs—O distances <3·7 Å; e.s.d.'s 0·013–0·019 Å

Cs(1)	O(3)	3·05	O(2^{i})	3·12	Aq(1^{i})	3·16
	O(5^{i})	3·20	O(4^{i})	3·31	O(4)	3·31
	O(5)	3·41	O(6)	3·47	Aq(2^{i})	3·54
Cs(2)	O(6^{ii})	3·02	O(1^{iii})	3·18	O(7)	3·21
	O(2^{iii})	3·22	O(4)	3·24	Aq(2^{iv})	3·25
	O(7^{ii})	3·30	O(2)	3·63	O(1)	3·64
Cs(3)	O(1^{v})	3·05	O(3^{v})	3·08	O(7^{ii})	3·12
	O(6)	3·16	O(1)	3·16	Aq(2^{vi})	3·19
	O(4)	3·31	Aq(1^{vii})	3·54		
Cs(4)	O(2^{viii})	3·07	O(5)	3·13	O(3^{viii})	3·15
	O(5^{i})	3·14	O(7^{i})	3·19	O(6)	3·28
	Aq(1^{viii})	3·31	O(3^{ix})	3·52		

(*b*) Aq—O distances (Å) and O—Aq—O angles (°) for possible hydrogen bonds; e.s.d.'s 0·02 Å and 0·7°

Aq(1)–O(2^{i})	2·70	Aq(2)–O(6^{iv})	2·69
Aq(1)–O(1^{x})	2·74	Aq(2)–O(5)	2·78
O(2^{i})–Aq(1)–O(1^{x})	103·9	O(5)–Aq(2)–O(6^{iv})	97·3

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Structure of Mercury(II) Iron(III) Fluoride Dihydrate, $HgFeF_5.2H_2O$

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Abstract. $M_r = 387·5$, orthorhombic, *Pbam*, $a = 10·711\,(2)$, $b = 6·638\,(1)$, $c = 4·008\,(1)$ Å, $U = 285·0$ Å^3, $Z = 2$, $D_x = 4·53$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 29·483$ mm^{-1}, $F(000) = 342$, $T = 293$ K. Final $R = 0·0291$ for 413 independent observed reflections. The structure consists of chains of *trans*-linked FeF_6 octahedra and rutile-type chains of $HgF_4(H_2O)_2$ octahedra running along [001], forming layers parallel to (100). These layers, related to the $MnAlF_5$ structure type, are connected to each other along [100] by strong O—H···F bonding.

Introduction. Very few inorganic and fluorinated compounds of mercury are known (Fourquet, Plet & De Pape, 1981). The present work on $HgFeF_5.2H_2O$ forms part of a research programme on such phases.

Experimental. Powdered samples are prepared from HgOHF and FeF_3 (1/1 ratio) in HF solutions (40%) at 473 K under 15 MPa or simply at ambient pressure, by evaporation of a saturated HF solution of HgOHF and FeF_3. Curiously, the best crystals were grown in HF solution (40%) at 473 K under 15 MPa from Hg_2F_2

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