(Johnson, 1965), and other unpublished programs written by one of the authors.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 atom not belonging to the V_2O_7 group was considered to be that of the water molecule Aq(1). Fig. 1 shows a stereoscopic view of the structure. The pairs of two V_2O_7 groups and two water molecules coupled by the centre of inversion at the cell centre (see Fig. 1) are arranged within a layer parallel to $(11\bar{1})$ to form a centred nearly rectangular net with vectors [112] and $[\bar{1}10]$ as unit-cell edges. The longitudinal direction of the pair runs parallel to [112]. Each layer is stacked on its underlying layer after having been translated by a vector $-\frac{1}{3}[112]$ relative to the latter; the layers are interleaved with Na^+ ions. The V_2O_7 group is twisted somewhat from the eclipsed conformation with the torsion angle about the V–V axis ranging from 18 to 33°; the bond lengths and angles are shown in Fig. 2. The Na^+ ions are coordinated irregularly by five or six O atoms with Na–O distances from 2·306 (4) to 2·777 (3) Å (Table 2), the next shortest Na–O being 3·274 (4) Å.

The H atoms could not be located in the difference-synthesis maps. To find hydrogen bonds around the water molecule, bond-valence sums were calculated (Donnay & Allmann, 1970) using the expression given by Brown & Wu (1976). The sum of the bond valences of O(5), 1·689, as well as the short distances $Aq(1^{ix})$–O(5) 2·682 (5) and Aq(1)–O(5) 2·839 (5) Å (symmetry code as in Table 2) show that O(5) is the acceptor of two hydrogen bonds. These distances are shorter than the shortest O–O distance [O(5)–O(5^{viii}) 2·970 Å] between different V_2O_7 groups and are in good agreement with the hydrogen-bonded Aq—O distances in $Na_4V_2O_7.18H_2O$ (Björnberg, 1979), where the H atoms were located in difference-synthesis maps by X-ray diffraction, and with the hydrogen-bonded O—O distances determined by neutron diffraction (Brown, 1976). Similar short Aq—O distances in $Ca_2V_2O_7.2H_2O$ were considered as suggesting well developed hydrogen bonds (Konnert & Evans, 1975). The bond-valence sums for the other O atoms range from 1·895 to 2·091.

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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42341 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrarubidium Divanadate Dihydrate

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Abstract. $Rb_4V_2O_7.2H_2O$, $M_r = 591·78$, triclinic, $P\bar{1}$, $a = 6·372$ (2), $b = 6·957$ (4), $c = 7·334$ (1) Å, $\alpha = 104·99$ (1), $\beta = 100·49$ (2), $\gamma = 94·54$ (1)°, $V = 306·09$ (8) Å^3, $Z = 1$, $D_x = 3·210$ Mg m^{-3}, λ(Cu $K\alpha_1$) = 1·540562, λ(Cu $K\alpha_2$) = 1·544390 Å for lattice constants, λ(Mo $K\bar{\alpha}$) = 0·71073 Å for intensity measurement, $\mu = 17·0$ mm^{-1}, $F(000) = 270$, $T = 298$ K. Final $R = 0·086$ for 1706 unique observed reflections. The

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V_2O_7 group has an inversion symmetry and hence a staggered conformation; V—O(br.)—V 180°, V—O(br.) 1·819 (2) Å. The Rb^+ ions are surrounded by seven or eight O atoms. The water molecule is hydrogen-bonded to two O atoms of V_2O_7 groups on one side and coordinated to two Rb^+ ions on the other.

Introduction. As part of our structural studies on alkali-metal vanadates, we reported the structures of $Na_4V_2O_7$ (Kato & Takayama, 1983), $Na_4V_2O_7.H_2O$ (tric.) (Kato & Takayama-Muromachi, 1985*b*) and $Cs_4V_2O_7.2H_2O$ (Kato & Takayama-Muromachi, 1985*a*). While the structures of divalent-metal divanadates have been widely studied [see *e.g.* Hawthorne & Calvo (1978) and the references therein], the compounds just mentioned and $Na_4V_2O_7.18H_2O$ (Björnberg, 1979) are the only alkali-metal divanadates whose structures have been determined. In the present work, we synthesized $Rb_4V_2O_7.2H_2O$ by evaporating an aqueous solution of $2Rb_2O.V_2O_5$ at 373 K and determined its crystal structure.

Experimental. Crystal of irregular rounded shape 0·3 × 0·2 × 0·15 mm, hygroscopic, enclosed in thin-wall (0·01 mm) glass capillary. Lattice constants from 51 reflections with $2\theta > 90°$ recorded on Weissenberg photographs with film radius 57·3 mm. Intensity measurement by Rigaku four-circle diffractometer up to $(\sin\theta)/\lambda = 0{\cdot}807$ Å^{-1}. ω-scanning, range $\Delta\omega = 1{\cdot}8° + 0{\cdot}5°\tan\theta$, speed 2° min^{-1}. R.m.s. deviations of *F*'s of three standard reflections measured 55 times throughout experiment 0·34–0·40%. 2697 reflections measured, 991 unobserved $[I < \sigma(I)]$, 1706 considered observed, index range $0 \leq h \leq 10$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$. No absorption correction. Structure solved by Patterson method. Atomic coordinates, anisotropic thermal parameters, a scale factor and a free parameter for extinction correction refined by least-squares method based on *F*, $R = 0{\cdot}086$, $wR = 0{\cdot}066$, $S = 3{\cdot}78$; weight $w = 1/\sigma^2(F)$. Extinction correction according to Zachariasen (1967, 1968) using a simplified expression $F_c = sF[1 + (g/\sin 2\theta)(1 + \cos^4 2\theta \cos^4 2\theta_M)(1 + \cos^2 2\theta \cos^2 2\theta_M)^{-1}F^2]^{-1/4}$, where $s = 2{\cdot}131$ (9), $g = 3\ (3) \times 10^{-7}$, $2\theta_M = 12{\cdot}17°$. $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·0004. $\Delta\rho = -3{\cdot}9$–$3{\cdot}8$ 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.

The rather large *R* values are to be attributed to the intensity data not being corrected for absorption. Computational absorption correction could not be performed as the irregular shape of the specimen in the capillary could not be measured with adequate accuracy. To form a specimen into spherical or equilateral shape was not practicable because it had to be manipulated in kerosene and put into the capillary as quickly as possible. The present compound was so highly hygroscopic that a small piece (~0·1 mm) of it would deliquesce within a few tens of seconds when exposed to the normal atmosphere.

Table 1. *Positional and equivalent isotropic thermal parameters of* $Rb_4V_2O_7.2H_2O$ *with e.s.d.'s in parentheses*

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

	x	*y*	*z*	B_{eq}(Å^2)
Rb(1)	0·3041 (2)	0·4111 (2)	0·1334 (2)	2·28 (3)
Rb(2)	0·7470 (2)	0·1115 (3)	0·3384 (2)	2·22 (3)
V	0·1862 (4)	−0·0957 (4)	0·1635 (3)	1·27 (4)
O(1)	0	0	0	3·2 (3)
O(2)	0·371 (2)	−0·199 (2)	0·054 (1)	2·1 (2)
O(3)	0·047 (2)	−0·264 (2)	0·237 (1)	2·4 (2)
O(4)	0·301 (2)	0·106 (2)	0·354 (1)	2·5 (2)
Aq	0·736 (2)	0·555 (2)	0·387 (2)	3·0 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°)

(*a*) Rb—O distances < 3·5 Å: e.s.d.'s 0·002 Å for Rb—O(1), 0·010–0·013 Å for the other distances

Rb(1)	O(3^{ii})	2·92	O(2^{ii})	2·93	Aq	2·96
	O(2^{vi})	2·97	O(4)	2·98	O(3^{viii})	3·07
	O(1)	3·143				
Rb(2)	O(4)	2·86	Aq	3·02	O(3^{v})	3·02
	O(2^{vi})	3·07	O(4^{v})	3·07	O(2)	3·12
	O(1^{iii})	3·165	O(3^{iii})	3·37		

(*b*) V—O distances and O—V—O angles; e.s.d.'s 0·002 Å for V—O(1), 0·009–0·010 Å for other distances, 0·4–0·5° for angles

V—O(2)	1·65	O(2)—V—O(3)	110·4
V—O(3)	1·67	O(2)—V—O(4)	110·7
V—O(4)	1·71	O(2)—V—O(1)	110·4
V—O(1)	1·819	O(3)—V—O(4)	110·5
		O(3)—V—O(1)	108·7
		O(4)—V—O(1)	106·0

(*c*) Aq—O distances < 3·4 Å and O—Aq—O angle; e.s.d.'s 0·015 Å and 0·5°

Aq—O(4^{iv})	2·68	O(4^{iv})—Aq—O(3^{i})	94·8
Aq—O(3^{i})	2·80		

Symmetry code: (i) $1+x$, $1+y$, z; (ii) x, $1+y$, z; (iii) $1+x$, y, z; (iv) $1-x$, $1-y$, $1-z$; (v) $1-x$, $-y$, $1-z$; (vi) $1-x$, $-y$, $-z$; (vii) $-x$, $-y$, $-z$.

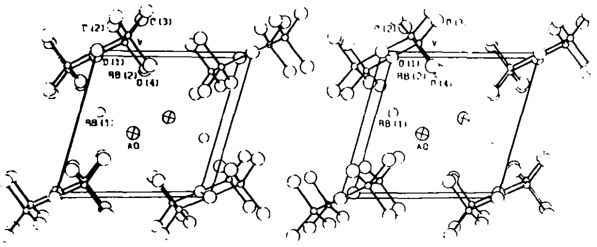

Fig. 1. Stereoscopic view of the structure along [100].

Discussion. The positional and equivalent isotropic thermal parameters are listed in Table 1.* The O atom not belonging to the V_2O_7 group was considered to be that of the water molecule, Aq. Fig. 1 shows the structure viewed along [100]. The interatomic distances and angles are listed in Table 2. Calvo & Faggiani (1975) and Hawthorne & Calvo (1978) surveyed the V—O bond lengths and V—O(br.)—V angles in various divalent-metal divanadates, $M_2V_2O_7$ and $M_2V_2O_7.2H_2O$, and found a general tendency that the average V—O(br.) bond length increases with decreasing V—O(br.)—V angle while the average terminal V—O bond length shows only small variations. The V_2O_7 group can take generally any intermediate conformation between eclipsed and staggered ones, and the V—O(br.)—V angle can vary in a wide range. The V_2O_7 group in the present compound has an inversion symmetry and hence an ideal staggered conformation with the V—O(br.)—V angle of 180°. As in $Cs_4V_2O_7.2H_2O$ (Kato & Takayama-Muromachi, 1985*a*), the V—O(br.) distance is longer by about 0·06 Å than those of the staggered V_2O_7 groups with V—O(br.)—V 180° in $Cd_2V_2O_7$ and $Mn_2V_2O_7$ [see Table VII and Fig. 4 in Hawthorne & Calvo (1978)]. The average V—O(br.) distances (1·812, 1·832 and 1·833 Å) in $Na_4V_2O_7$ (Kato & Takayama, 1983) and $Na_4V_2O_7.H_2O$ (tric.) (Kato & Takayama-Muromachi, 1985*b*) are also longer than those in $M_2V_2O_7$ compounds with similar V—O(br.)—V angles (149·4, 133·4 and 125·6°, respectively). The longer V—O(br.) distances are thus a general feature of the V_2O_7 groups in alkali-metal divanadates, $R_4V_2O_7$, and their hydrates, and may probably be related to the coordination number of the O(br.) atom. The coordination number is in general, as a consequence of a higher cation-to-anion ratio, greater in the $R_4V_2O_7$ structure than in $M_2V_2O_7$. The V—O(br.) bond will be weakened just to that extent as the bond valence of O(br.) must be allotted to the surrounding cations. For example, the O(br.) atom in $Rb_4V_2O_7.2H_2O$ has two V and four Rb neighbours, while those in $Cd_2V_2O_7$ and $Mn_2V_2O_7$ have no cation neighbours except for two V atoms (Hawthorne & Calvo, 1978). The long V—O(br.) distance in $Rb_4V_2O_7.2H_2O$ may be also due to the steric influence of the four large Rb^+ ions which surround the V_2O_7 group as if forcing it into the hollow space around the O(br.) atom.

The water molecule is attached on one side to two O atoms of V_2O_7 groups and binds them through hydrogen bonds to form a linear chain parallel to [001]. On the other side, it is coordinated to two Rb^+ ions and thus exhibits a nearly tetrahedral arrangement of neighbours, a typical behaviour of water molecules in hydrated oxy-salts as pointed out by Wells (1975). The short Aq—O distances listed in Table 2 correspond to the hydrogen-bonded O···O distances determined by neutron diffraction (Brown, 1976), and are thus acceptable as such distances.

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Trirubidium Vanadate Tetrahydrate

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(*Received* 22 *May* 1985; *accepted* 2 *July* 1985)

Abstract. $Rb_3VO_4.4H_2O$, $M_r = 443·40$, orthorhombic, *Pbca*, $a = 16·255$ (1), $b = 17·771$ (1), $c = 7·002$ (1) Å, $V = 2022·7$ (3) Å^3, $Z = 8$, $D_x = 2·912$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1·540562$, $\lambda(\mathrm{Cu}\ K\alpha_2) = 1·544390$ Å for lattice constants, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0·71073$ Å for intensity measurement, $\mu = 15·0$ mm^{-1}, $F(000) = 1648$, $T =$