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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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42353 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trirubidium Vanadate Tetrahydrate

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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}, 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, μ = 15·0 mm^{-1}, *F*(000) = 1648, *T* =

0108-2701/85/101415-03\$01.50

298 K. Final $R = 0{\cdot}074$ for 1637 unique observed reflections. The Rb^+ ions are surrounded by eight or nine O atoms. A network of hydrogen bonds is formed between the water molecules and the O atoms of the VO_4 group.

Introduction. In the course of our structural investigations on alkali-metal vanadates, we reported the structures of β-$NaVO_3$, NaV_2O_7, $Cs_4V_2O_7.2H_2O$, $K_5V_3O_{10}$, $Na_5V_3O_{10}.2H_2O$, $Na_4V_2O_7.H_2O$ (tric.) and $Rb_4V_2O_7.2H_2O$ (Kato & Takayama, 1983, 1984; Kato & Takayama-Muromachi, 1985*a,b,c,d,e*). In the present work, we have determined the structure of the title compound which was obtained from aqueous solution of $3Rb_2O.V_2O_5$ by evaporation at 373 K as one of two unknown phases. The other phase was identified as $Rb_4V_2O_7.2H_2O$.

There are few studies on the structures of tri-alkali-metal vanadates and their hydrates. Li_3VO_4 is polymorphic and isomorphic with Li_3PO_4 (Tarte, 1967; West & Glasser, 1972; West, 1975), and the structure of low-temperature Li_3VO_4 was refined by Shannon & Calvo (1973). Na_3VO_4 is also polymorphic, and its high-temperature modification was reported to be isostructural with Na_2CaSiO_4 (Le Flem, Olazcuaga, Parant, Reau & Fouassier, 1971; Barker & Hooper, 1973). The structure of $Na_3VO_4.12H_2O$, in fact $Na_3VO_4(NaOH)_{0\text{-}0.25}.12H_2O$, was determined by Tillmanns & Baur (1971).

Experimental. Crystal of irregular rounded shape $0{\cdot}4 \times 0{\cdot}15 \times 0{\cdot}15$ mm, hygroscopic, enclosed in thin-wall (0·01 mm) glass capillary. Lattice constants from 37 *hk*0 and 17 *h*0*l* 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 $\Delta\omega = 1{\cdot}3° + 0{\cdot}5°\tan\theta$, speed 2° min^{-1}. R.m.s. deviations of *F*'s of three standard reflections measured 93 times throughout experiment 0·5–1·1%; frequent redetermination of the orientation matrix necessary. 4481 reflections measured, 2844 unobserved $[I < \sigma(I)]$, 1637 considered observed, index range $0 \le h \le 26$, $0 \le k \le 28$, $0 \le l \le 11$. 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*, $R = 0{\cdot}074$, $wR = 0{\cdot}040$, $S = 1{\cdot}81$; 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 $s = 0{\cdot}502\ (2)$, $g = 1{\cdot}23\ (4) \times 10^{-6}$, $2\theta_M = 12{\cdot}17°$. $(\Delta/\sigma)_{\max}$ in final refinement cycle 0·0005. $\Delta\rho = -1{\cdot}4$–$1{\cdot}6$ 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 due to the lack of absorption correction. The latter 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* $Rb_3VO_4.4H_2O$ *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)	0·09270 (9)	0·17089 (7)	0·0688 (2)	2·13 (3)
Rb(2)	0·30370 (9)	0·19178 (8)	0·3665 (2)	2·32 (3)
Rb(3)	0·41244 (9)	0·05069 (8)	0·7438 (3)	3·03 (4)
V	0·1131 (1)	0·1260 (1)	0·5778 (4)	1·53 (4)
O(1)	0·0196 (5)	0·1699 (5)	0·515 (1)	2·1 (2)
O(2)	0·1779 (5)	0·1907 (4)	0·680 (1)	2·0 (2)
O(3)	0·0918 (6)	0·0567 (5)	0·737 (2)	3·2 (2)
O(4)	0·1602 (5)	0·0911 (5)	0·379 (1)	2·0 (2)
Aq(1)	0·4382 (5)	0·2213 (4)	0·673 (1)	1·9 (2)
Aq(2)	0·4516 (5)	0·0874 (4)	0·283 (2)	2·4 (2)
Aq(3)	0·2866 (5)	0·0050 (6)	0·468 (1)	2·7 (2)
Aq(4)	0·2775 (5)	0·1401 (5)	0·956 (1)	2·8 (2)

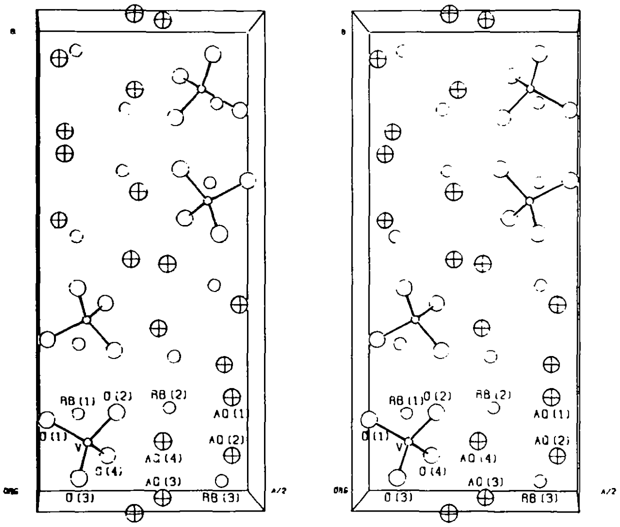

Fig. 1. Stereoview of the structure along [001] showing one half of the unit cell.

Discussion. The positional and equivalent isotropic thermal parameters are listed in Table 1.* The O atoms not belonging to the VO_4 group were considered to be those of water molecules, Aq(1)–Aq(4). Fig. 1 shows the structure viewed along [001]. Interatomic distances and angles are listed in Table 2. The Rb(1) ion is coordinated by six O atoms of three neighbouring VO_4 groups and holds them together to form a column parallel to [001]. The Rb(2) ion is attached to the side of the column through contacts with three O atoms of VO_4 groups. The columns are connected to each other partly by Rb(3) through Rb—O ionic bonds, but mainly through sharing of water molecules between the coordination groups of Rb^+ ions. The complex network of hydrogen bonds between the water molecules and the O atoms of VO_4 groups contributes much to the bonding between the columns. The short Aq—O and Aq—Aq distances suggesting hydrogen bonds are listed in Table 2; they correspond to the hydrogen-bonded O···O distances determined by neutron diffraction (Brown, 1976). The Aq(3) molecule forms two hydrogen bonds with the O(4) and O(3^{viii}) atoms, and also operates as the acceptor of a hydrogen bond with Aq(4^{viii}) (symmetry code as in Table 2). The long, and hence weakened, V—O(1) bond may be related to the multiple role of O(1) as a neighbour of three Rb^+ ions and an acceptor of three hydrogen bonds.

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

(*a*) Rb—O distances <3·6 Å; e.s.d.'s 0·008–0·010 Å

Rb(1)	O(4)	2·82	Aq(2^{i})	2·92	O(2^{ii})	2·93
	O(2^{iii})	3·07	O(3^{iii})	3·08	O(1^{ii})	3·09
	Aq(4^{iii})	3·15	Aq(1^{i})	3·16	O(1)	3·34
Rb(2)	O(4)	2·94	Aq(1^{ii})	3·00	O(2)	3·00
	Aq(4^{iii})	3·05	Aq(4^{ii})	3·08	Aq(2)	3·09
	Aq(1)	3·11	O(2^{ii})	3·20	Aq(3)	3·41
Rb(3)	O(3^{iv})	2·92	Aq(3)	2·93	O(4^{v})	2·94
	Aq(4)	3·09	Aq(1)	3·10	O(1^{iv})	3·22
	Aq(2^{vi})	3·31	Aq(2)	3·35		

(*b*) V—O distances and O—V—O angles; e.s.d.'s 0·008–0·010 Å and 0·4–0·5°

V—O(3)	1·70	O(3)—V—O(4)	111·3
V—O(4)	1·70	O(3)—V—O(2)	109·6
V—O(2)	1·72	O(3)—V—O(1)	108·0
V—O(1)	1·76	O(4)—V—O(2)	108·0
		O(4)—V—O(1)	110·2
		O(2)—V—O(1)	109·7

(*c*) Aq—O(Aq) distances <3·3 Å and O—Aq—O(Aq) angles; e.s.d.'s 0·011–0·014 Å and 0·4–0·5°

Aq(1)—O(1^{vii})	2·69	O(1^{vii})—Aq(1)—O(1^{iv})	113·4
Aq(1)—O(1^{iv})	2·71		
Aq(2)—O(3^{viii})	2·67	O(3^{viii})—Aq(2)—O(1^{ix})	121·3
Aq(2)—O(1^{ix})	2·78		
Aq(3)—O(4)	2·64	O(4)—Aq(3)—O(3^{viii})	130·3
Aq(3)—O(3^{viii})	2·78		
Aq(3)—Aq(4^{viii})	2·78		
Aq(4)—O(2)	2·67	O(2)—Aq(4)—Aq(3^{v})	96·1
Aq(4)—Aq(3^{v})	2·78		

Symmetry code: (i) $-\frac{1}{2}+x, y, \frac{1}{2}-z$; (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $x, y, -1+z$; (iv) $\frac{1}{2}+x, y, \frac{3}{2}-z$; (v) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (vi) $1-x, -y, 1-z$; (vii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (viii) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (ix) $\frac{1}{2}+x, y, \frac{1}{2}-z$.

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