

Fig. 2. V—O distances (Å) and V—O—V angle ($^{\circ}$) in V_3O_{10} group. E.s.d.'s are 0.002–0.004 Å and 0.1° . V(1) lies on a twofold rotation axis. O—V(1)—O angles are $106.5(2)$ – $110.4(3)^{\circ}$, O—V(2)—O $108.0(2)$ – $111.5(2)^{\circ}$.

Table 2. Na—O distances (Å) less than 3.0 Å

E.s.d.'s range from 0.003 to 0.006 Å.

Na(1)	O(1 ^{vi})	2.376	O(5 ⁱⁱⁱ)	2.392	O(3)	2.452
Na(2)	O(1 ⁱⁱ)	2.352	Aq(1)	2.374	O(3 ⁱ)	2.441
	O(1 ^v)	2.524	O(5 ^{iv})	2.681	O(5 ^{vii})	2.949
Na(3)	O(3 ^v)	2.364	O(4 ⁱⁱⁱ)	2.413	O(5 ^{vi})	2.431
	O(4 ^v)	2.455	Aq(1)	2.495	O(2)	2.631

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

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 expressions given by Brown & Wu (1976). The sums of bond valences of O(2) and O(4), 1.904 and 1.829 respectively, suggest that these atoms are possible acceptors of the hydrogen

bonds. The distances Aq(1)—O(2^v) 2.953 (6) and Aq(1)—O(4^{iv}) 3.049 (6) Å (symmetry code as in Table 2) correspond to those of weak hydrogen bonds (Brown, 1976), but are still shorter than the shortest O—O distance 3.075 (5) Å between different V_3O_{10} groups in the present compound. The bond-valence sums for the other O atoms range from 1.997 to 2.062.

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Acta Cryst. (1985). **C41**, 1411–1413

Triclinic Tetrasodium Divanadate Hydrate

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(Received 7 May 1985; accepted 27 June 1985)

Abstract. $Na_4V_2O_7 \cdot H_2O$ (tric.), $M_r = 323.85$, triclinic, $P\bar{1}$, $a = 6.960(1)$, $b = 7.4025(5)$, $c = 8.3129(3)$ Å, $\alpha = 85.395(4)$, $\beta = 85.712(4)$, $\gamma = 75.37(1)^{\circ}$, $V = 412.40(6)$ Å³, $Z = 2$, $D_x = 2.608$ Mg m⁻³, $Cu K\alpha_1$, $\lambda = 1.540562$, $Cu K\alpha_2$, $\lambda = 1.544390$ Å for lattice constants, $Mo K\alpha$, $\lambda = 0.71073$ Å for intensity

measurement, $\mu = 2.41$ mm⁻¹, $F(000) = 312$, $T = 298$ K, final $R = 0.044$ for 2111 unique observed reflections. The V_2O_7 group has a nearly eclipsed conformation with V—O—V angle $125.6(2)^{\circ}$. The V_2O_7 groups and water molecules are arranged in layers parallel to (111), stacked with a translation of

0108-2701/85/101411-03\$01.50

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$\frac{1}{3}[112]$ between adjacent layers. The Na^+ ions are situated between the layers and are surrounded by five or six O atoms.

Introduction. As part of our studies on alkali-metal vanadates, we reported the structures of $\text{Na}_4\text{V}_2\text{O}_7$ obtained from its melt by slow cooling (Kato & Takayama, 1983) and of $\text{Cs}_4\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ crystallized from aqueous solution (Kato & Takayama-Muromachi, 1985a). As $\text{Na}_4\text{V}_2\text{O}_7$ is known to be dimorphic (Barker & Hooper, 1983), we tried to get single crystals of its low-temperature modification by evaporating an aqueous solution of $2\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$ at 373 K, but we obtained instead of the intended product two unknown phases, which proved to be $\text{Na}_4\text{V}_2\text{O}_7 \cdot \text{H}_2\text{O}$ and $\text{Na}_5\text{V}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ by structure determinations. During our further investigations, $\text{Na}_4\text{V}_2\text{O}_7 \cdot \text{H}_2\text{O}$ was found to be dimorphic. The modification for which the structure is reported here is triclinic, while the other crystallizes in space group $P2_1/c$ with $a = 8.4367$ (4), $b = 8.6641$ (6), $c = 11.2554$ (9) Å and $\beta = 95.161$ (7)°. The structure determination of the monoclinic phase is in progress. The structure of $\text{Na}_5\text{V}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ is reported in the preceding paper (Kato & Takayama-Muromachi, 1985b). In contrast to alkali-metal divanadates, the structures of the divanadates of divalent metals have been widely studied; see e.g. Hawthorne & Calvo (1978) and references therein.

Experimental. Crystal of irregular shape, $0.2 \times 0.2 \times 0.3$ mm, hygroscopic, enclosed in thin-wall (0.01 mm) glass capillary. Lattice constants from 99 reflections with $2\theta > 90^\circ$ recorded on Weissenberg photographs with film radius 57.3 mm. Intensity measurement by Rigaku four-circle diffractometer up to $(\sin\theta)/\lambda = 0.756 \text{ \AA}^{-1}$. $2\theta/\omega$ scan for $2\theta \geq 30^\circ$, ω scan for $2\theta < 30^\circ$, scan range $\Delta\omega = (1.2 + 0.5 \tan\theta)^\circ$, speed 2° min^{-1} . R.m.s. deviations of F 's of three standard reflections measured 61 times throughout experiment, 0.53–0.62%. 2993 reflections measured, 882 unobserved [$I < \sigma(I)$], 2111 considered observed, index range $0 \leq h \leq 10$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$. 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 , $R = 0.044$, $wR = 0.037$, $S = 1.91$; $w = 1/\sigma^2(F)$. Extinction correction according to Zachariasen (1967, 1968) using a simplified expression $F_c = sF[1 + (g/\sin 2\theta)(1 + \cos^2 2\theta)(1 + \cos^2 2\theta)^{-1/4}]^{-1/4}$, where $s = 2.083$ (4) and $g = 9.0$ (4) $\times 10^{-6}$. Max. Δ/σ in final refinement cycle 0.001. $\Delta\rho = -0.86$ – 0.62 e \AA^{-3} . Atomic scattering factors of Cromer & Mann (1968), dispersion corrections of Cromer & Liberman (1970). Computer programs used: *RSLC3* in *UNICS* system (Sakurai, 1967), *ORFFE* (Busing, Martin & Levy, 1964), version 2 of *ORTEP*

Table 1. Positional and equivalent isotropic thermal parameters of $\text{Na}_4\text{V}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (tric.) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Na(1)	0.9094 (3)	0.0333 (3)	0.2932 (2)	1.62 (3)
Na(2)	0.8559 (3)	0.5116 (3)	0.2954 (2)	1.91 (4)
Na(3)	0.6768 (3)	0.3109 (3)	0.9601 (2)	1.69 (3)
Na(4)	0.5074 (3)	0.1240 (3)	0.6687 (2)	1.71 (3)
V(1)	0.1887 (1)	0.1963 (1)	0.04324 (9)	0.92 (1)
V(2)	0.4086 (1)	0.3623 (1)	0.30902 (9)	0.95 (1)
O(1)	0.2066 (5)	0.1873 (4)	-0.1587 (4)	1.44 (6)
O(2)	0.2550 (5)	-0.0170 (4)	0.1385 (4)	1.66 (6)
O(3)	-0.0481 (4)	0.2899 (4)	0.1062 (4)	1.34 (5)
O(4)	0.3521 (5)	0.3377 (4)	0.1028 (4)	1.39 (5)
O(5)	0.1969 (5)	0.4038 (5)	0.4269 (4)	2.33 (7)
O(6)	0.5006 (5)	0.5524 (5)	0.2917 (4)	2.06 (6)
O(7)	0.5682 (5)	0.1688 (4)	0.3771 (4)	1.58 (6)
Aq(1)	0.0634 (6)	0.7912 (5)	0.4786 (4)	2.24 (7)

Table 2. Na–O distances (Å)

E.s.d.'s range from 0.003 to 0.004 Å.

Na(1)	Aq(1 ^{iv}) 2.360	O(1 ^{viii}) 2.380	O(7) 2.407
	O(3 ⁱⁱⁱ) 2.419	Aq(1 ^v) 2.428	O(2 ⁱⁱ) 2.596
Na(2)	O(3 ⁱⁱⁱ) 2.306	O(1 ^{vi}) 2.372	O(6) 2.416
	O(5 ^v) 2.418	O(5 ⁱⁱⁱ) 2.599	Aq(1 ^v) 2.777
Na(3)	O(3 ⁱⁱⁱ) 2.309	O(2 ^{vii}) 2.310	O(4 ⁱ) 2.442
	O(6 ^v) 2.519	O(4 ^v) 2.572	
Na(4)	O(2 ^{vii}) 2.337	O(1 ⁱ) 2.414	O(7 ^{vii}) 2.420
	O(6 ^v) 2.430	O(7) 2.439	

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

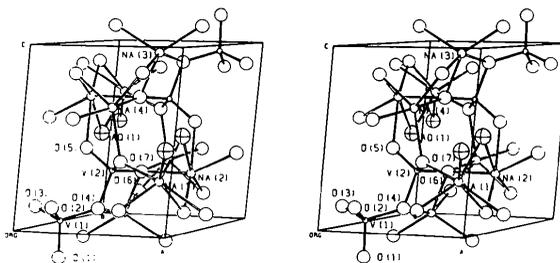


Fig. 1. Stereoview of the $\text{Na}_4\text{V}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (tric.) structure. Besides two V_2O_7 groups and two water molecules within the unit cell, two additional water molecules and those O atoms of the V_2O_7 groups in neighbouring unit cells are drawn that complete the coordination polyhedra of the Na^+ ions.

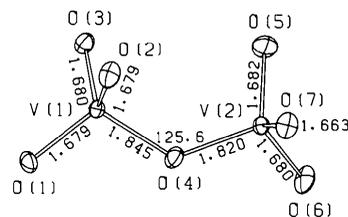


Fig. 2. V–O distances (Å) and angle ($^\circ$) in V_2O_7 group. E.s.d.'s are 0.003 Å and 0.2° . O–V(1)–O angles are 106.6 (2)– 112.2 (2)°, O–V(2)–O 103.2 (2)– 113.8 (2)°.

(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

* 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.

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 $Na_4V_2O_7 \cdot 18H_2O$ (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 $Ca_2V_2O_7 \cdot 2H_2O$ 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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Acta Cryst. (1985). **C41**, 1413–1415

Tetrarubidium Divanadate Dihydrate

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(Received 22 May 1985; accepted 2 July 1985)

Abstract. $Rb_4V_2O_7 \cdot 2H_2O$, $M_r = 591.78$, 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) Å³, $Z = 1$, $D_x = 3.210$ Mg m⁻³, $\lambda(Cu K\alpha_1) = 1.540562$, $\lambda(Cu K\alpha_2) = 1.544390$ Å for lattice constants, $\lambda(Mo K\alpha) = 0.71073$ 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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