substrates or of the presence of Ag on polytypism of PbI_2 were observed. The multilayer polytypes reported here were usually found occurring in the presence of two basic polytypes $2H$ and $4H$ and/or $12R$. This agrees well with the results reported earlier on other MX_2 compounds where multilayer polytypes were considered as structures intermediate between two different structures (Pałosz, 1983; Pałosz & Przedmojski, 1984): polytypes do not originate from a single structure, they form only when two different basic structures grow simultaneously.

One important fact indicating a difference between isostructural crystals of CdI_2 and PbI_2 should here be stressed. These two materials have similar construction and similar basic structures ($2H$ and $4H$) but in the case of PbI_2 the polytype $12R$ is the third basic structure while this polytype occurs only occasionally in CdI_2. The multilayer polytypes having the stackings $f2$–$f2f4$ occur very rarely in CdI_2 but are frequent in PbI_2: the polytype $18R$: $f2f2f4$ has never been found in CdI_2 but occurs frequently in PbI_2. The above differences between CdI_2 and PbI_2 may be very important in the analysis of the forces governing polytype structure formation.

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Pentasodium Trivanadate Dihydrate

By Katsuo Kato and Eiji Takayama-Muromachi

National Institute for Research in Inorganic Materials, 1–1 *Namiki, Sakura-mura, Niihari-gun, Ibaraki-ken* 305, *Japan*

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Abstract. $Na_5V_3O_{10}.2H_2O$, $M_r = 463\cdot80$, orthorhombic, $C222_1$, $a = 5\cdot9632\ (6)$, $b = 9\cdot3751\ (5)$, $c = 20\cdot7537\ (8)$ Å, $V = 1160\cdot2\ (1)$ Å^3, $Z = 4$, $D_x = 2\cdot655$ Mg m^{-3}, Cu $K\alpha_1$, $\lambda = 1\cdot540562$, Cu $K\alpha_2$, $\lambda = 1\cdot544390$ Å for lattice constants, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71073$ Å for intensity measurement, $\mu = 2\cdot53$ mm^{-1}, $F(000) = 896$, $T = 298$ K, final $R = 0\cdot030$ for 1301 unique observed reflections. The linear chain of the V_3O_{10} group has twofold rotation symmetry and runs parallel to [001]. The V—O—V angle is 122·8 (1)°. The Na^+ ions are situated between the layers of V_3O_{10} groups and are surrounded by six O atoms in an octahedral arrangement.

Introduction. In the course of our studies on alkali-metal vanadates, we tried to prepare single crystals of the low-temperature modification of anhydrous $Na_4V_2O_7$ by evaporating an aqueous solution of $2Na_2O.V_2O_5$ at 373 K, but we obtained two unknown phases instead of the aimed product. One of them was revealed to be $Na_5V_3O_{10}.2H_2O$ by the following structure determination. The structure of the other phase, $Na_4V_2O_7.H_2O$ (tric.), is reported in the following paper (Kato & Takayama-Muromachi, 1985*b*).

While single crystals of $K_5V_3O_{10}$ could be obtained by evaporating aqueous solution and used as specimens for a structure determination (Kato & Takayama-

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Muromachi, 1985*a*); trials to synthesize anhydrous $Na_5V_3O_{10}$ by an analogous method at 393 and 403 K were not successful. The latter compound may thus be really unstable at these lower temperatures; it is already established that it does not exist at higher temperatures (Roth, Negas & Cook, 1981).

Experimental. Crystal of irregular shape, 0·2 × 0·2 × 0·3 mm, hygroscopic, enclosed in thin-wall (0·01 mm) glass capillary. Lattice constants from 42 $0kl$ and 15 $h0l$ reflections with $2\theta > 90°$ recorded on Weissenberg photographs with film radius 57·3 mm. Intensity measurement by Rigaku four-circle diffractometer up to $(\sin\theta)/\lambda = 0{\cdot}809$ Å^{-1}; $2\theta/\omega$ scan for $2\theta \geq 30°$, ω scan for $2\theta < 30°$, scan range $\Delta\omega = (1{\cdot}2 + 0{\cdot}5\tan\theta)$,° speed 2° min^{-1}. R.m.s. deviations of F's of three standard reflections measured 32 times throughout experiment, 0·33–0·45%. 1457 reflections measured, 156 unobserved $[I < \sigma(I)]$, 1301 considered observed, index range $0 \leq h \leq 9$, $0 \leq k \leq 15$, $0 \leq l \leq 33$. 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, $R = 0{\cdot}030$, $wR = 0{\cdot}034$, $S = 3{\cdot}26$; $w = 1/\sigma^2(F)$. Extinction correction according to Zachariasen (1967, 1968) using a simplified expression

$$F_c = sF[1+(g/\sin2\theta)(1+\cos^4 2\theta\cos^4 2\theta_M) \times (1+\cos^2 2\theta\cos^2 2\theta_M)^{-1}F^2]^{-1/4},$$

where $s = 3{\cdot}924\ (9)$, $g = 1{\cdot}31\ (5) \times 10^{-5}$ and $2\theta_M = 12{\cdot}17°$. Max. Δ/σ in final refinement cycle 0·0007. $\Delta\rho = -0{\cdot}63$–$0{\cdot}53$ 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 atom not belonging to the V_3O_{10} group was considered to be that of the water molecule Aq(1). Fig. 1 shows the structure viewed along [100]. The V_3O_{10} groups are arranged together with the water molecules to form a layer parallel to (010). The Na^+ ions are found between the layers holding them together. Though the space group $C222_1$ could be established unambiguously by the systematic absences of reflections, the structure has an approximate symmetry of *Cmcm*. In contrast with the trivanadate group in $K_5V_3O_{10}$ (Kato & Takayama-Muromachi, 1985*a*), which is bent at the central V atom, the V_3O_{10} group in $Na_5V_3O_{10}.2H_2O$ takes the shape of a linear chain running parallel to [001] with each VO_4 tetrahedron being in a nearly eclipsed position relative to its neighbour(s). The P_3O_{10} groups in two phases of $Na_5P_3O_{10}$ (Davies & Corbridge, 1958; Corbridge, 1960) are also linear, but the PO_4 tetrahedra are oriented in a staggered conformation relative to each other. Bond lengths and angles in the V_3O_{10} group are shown in Fig. 2. Na(1) and Na(3) are coordinated nearly octahedrally to six O atoms respectively, while Na(2) is surrounded by six O atoms rather irregularly. The Na—O distances are listed in Table 2.

Table 1. *Positional and equivalent isotropic thermal parameters of* $Na_5V_3O_{10}.2H_2O$ *with e.s.d.'s in parentheses*

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

	x	y	z	$B_{\rm eq}$(Å^2)
Na(1)	0·4891 (7)	0	0	1·40 (4)
Na(2)	−0·0260 (6)	0·8134 (2)	0·05967 (8)	2·51 (5)
Na(3)	0·0021 (6)	0·4912 (2)	0·16394 (7)	1·86 (3)
V(1)	0	0·10191 (9)	0·25	0·91 (1)
V(2)	0·0086 (2)	0·13839 (6)	0·09555 (3)	0·88 (1)
O(1)	0·0596 (6)	0·2706 (3)	0·0442 (1)	1·84 (7)
O(2)	0·0021 (8)	0·2127 (3)	0·1794 (1)	1·21 (4)
O(3)	0·2123 (7)	0·0163 (4)	0·0870 (2)	1·64 (7)
O(4)	0·2228 (5)	−0·0040 (3)	0·2508 (3)	1·65 (5)
O(5)	0·2377 (7)	0·0618 (4)	0·4204 (2)	1·81 (7)
Aq(1)	−0·0085 (8)	0·7568 (3)	0·1710 (1)	1·88 (5)

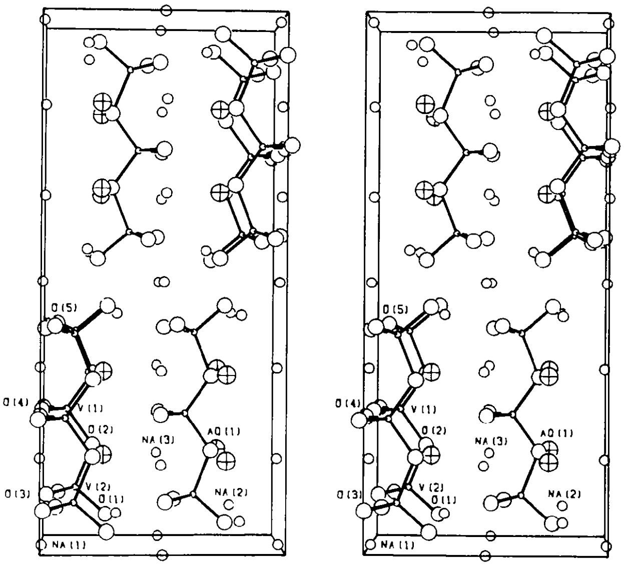

Fig. 1. Stereoview of the $Na_5V_3O_{10}.2H_2O$ structure along [100].

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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 42340 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

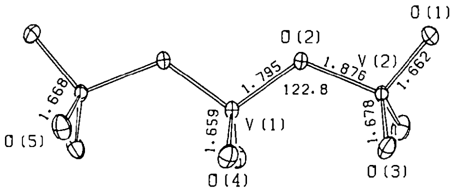

Fig. 2. V—O distances (Å) and V—O—V angle (°) in V_3O_{10} group. E.s.d.'s are 0·002–0·004 Å and 0·1°. V(1) lies on a twofold rotation axis. O—V(1)—O angles are 106·5 (2)–110·4 (3)°, O—V(2)—O 108·0 (2)–111·5 (2)°.

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^{vii})	2·413	O(5^{vii})	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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Triclinic Tetrasodium Divanadate Hydrate

BY KATSUO KATO AND EIJI TAKAYAMA-MUROMACHI

National Institute for Research in Inorganic Materials, 1-1 *Namiki, Sakura-mura, Niihari-gun, Ibaraki-ken* 305, *Japan*

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Abstract. $Na_4V_2O_7.H_2O$(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)°, $V = 412·40$ (6) Å^3, $Z = 2$, $D_x = 2·608$ Mg m^{-3}, Cu $K\alpha_1$, $\lambda = 1·540562$, Cu $K\alpha_2$, $\lambda = 1·544390$ Å for lattice constants, Mo $K\bar{\alpha}$, $\lambda = 0·71073$ 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)°. The V_2O_7 groups and water molecules are arranged in layers parallel to $(11\bar{1})$, stacked with a translation of

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