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Dipotassium tetrasodium decavanadate octadecahydrate

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The title double salt, $K_2Na_4[V_{10}O_{28}]\cdot18H_2O$, crystallizes with a decavanadate polyanion that has twofold crystallographic symmetry. All atoms in the structure are on general positions, except two Na atoms which are located on a twofold axis. In the crystal structure, chains made up of edge- and face-sharing $[KO_9]$ and $[NaO_6]$ polyhedra are interconnected by the decavanadate anions to form a three-dimensional network. The decavanadate polyanion exhibits the typical ranges in V$\cdots$V and the four types of V—O distances.

Comment

Recently, some alkali metal decavanadate double salts, *viz.* $\{[LiNa_2(H_2O)_9]_2[V_{10}O_{28}]\}_n$ (Ma *et al.*, 2005) and $Na_{5.22}Li_{0.78}$-$[V_{10}O_{28}]\cdot20H_2O$ (Ksiksi *et al.*, 2005), have been reported. We chose the double salt system of K^+ and Na^+ and succeeded in growing crystals of $K_4Na_2[V_{10}O_{28}]\cdot10H_2O$ (Lee & Joo, 2003) and $K_4Na[HV_{10}O_{28}]\cdot10H_2O$ (Lee & Joo, 2004), the latter being the first monoprotonated decavanadate species to be reported in the solid state. $K_4Na_2[V_{10}O_{28}]\cdot10H_2O$ crystallizes in space group $P\bar{1}$ and its decavanadate polyanion has $\bar{1}$ symmetry, whereas $K_4Na[HV_{10}O_{28}]\cdot10H_2O$ crystallizes in space group $P2/n$ and its decavanadate anion has 2 symmetry. In the course of these investigations, we obtained the title compound, $K_2Na_4[V_{10}O_{28}]\cdot18H_2O$, (I), at a pH of 6.8, and present its crystal ctructure here.
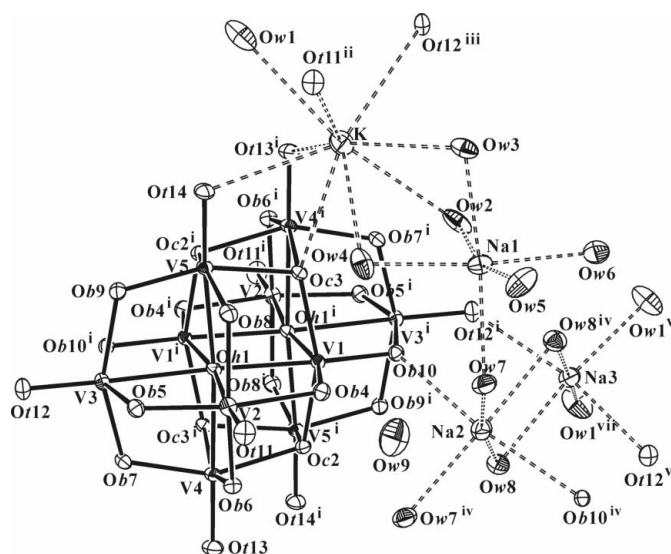
Figure 1
Part of the structure of (I), showing the coordination polyhedra around the cations and the decavanadate polyanion. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} + x, 1/2 + y, z$; (iv) $1 - x, y, \frac{1}{2} - z$; (v) $x, 1 - y, z - \frac{1}{2}$. (vi) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$; (vii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$.]
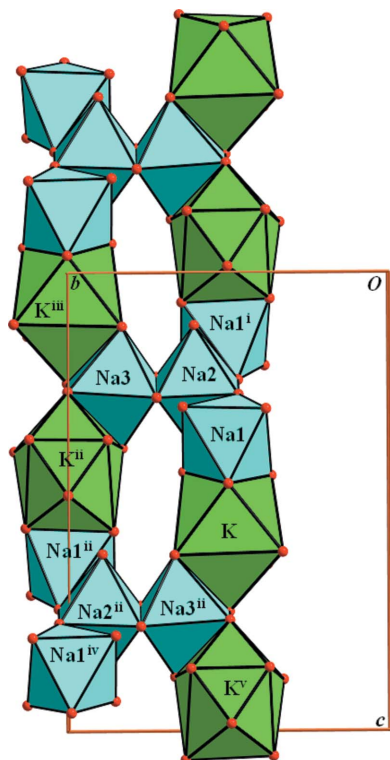
Figure 2
A polyhedral model, in a projection down the *a* axis, for the linear network made up of [KO$_9$] and [NaO$_6$] polyhedra. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (v) $2 - x, y, \frac{3}{2} - z$.]
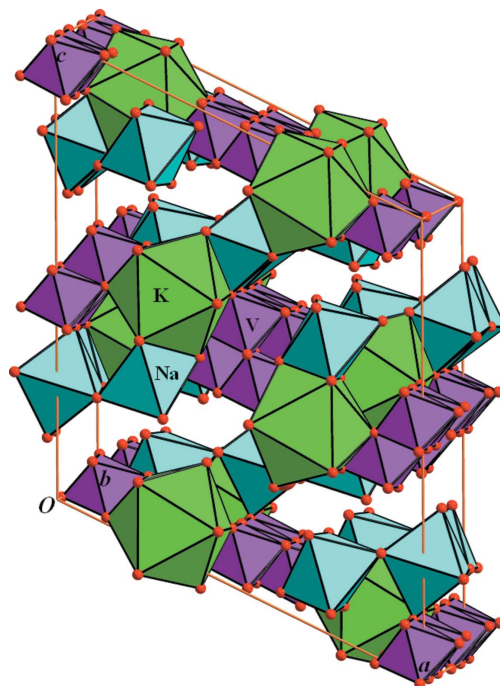

Figure 3
A polyhedral representation of the unit-cell contents of (I), viewed approximately down the *b* axis.

Fig. 1 shows part of the structure of (I) and the labelling scheme for the decavanadate anion. The asymmetric unit in the decavanadate polyanion consists of five independent [VO$_6$] octahedra sharing edges; the crystallographic twofold axis generates the other half of the polyanion. The V···V distances within the polyanion are in the range 3.060 (1)– 3.169 (1) Å; the V—O bond lengths range between 1.607 (3) and 2.331 (3) Å and are given in Table 1. The O atoms in the decavanadate anions are the same terminal (O$_t$) and bridging (O$_b$) types as those classified in the previous report by Lee *et al.* (2003). All atoms in (I) are on general positions, except atoms Na2 and Na3, which are located on a twofold axis.

The K$^+$ ion is coordinated by nine O atoms, [K(O$_c$)(O$_t$)$_4$(O$_w$)$_4$], and the three Na$^+$ ions are coordinated by six O atoms each, *viz.* [Na1(O$_w$)$_6$], [Na2(O$_w$)$_4$(O$_b$)$_2$] and [Na3(O$_w$)$_4$(O$_t$)$_2$]. The bond-valence sum (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) of K$^+$ is 0.939, and those of atoms Na1$^+$, Na2$^+$ and Na3$^+$ are 1.203, 1.136 and 1.224, respectively.

The O$_w$9 water molecule does not coordinate to any cations, but it is hydrogen bonded to atom O$_b$6($1 - x, y, \frac{1}{2} - z$) at a distance of 3.054 (6) Å. By sharing edges and faces, the [KO$_9$] and [NaO$_6$] polyhedra form linear chains extending parallel to [101] (Fig. 2). These chains are made up of eight-membered rings, K/Na1/Na2/Na3/K^{ii}/Na1^{ii}/Na^{ii}/Na3^{ii} (symmetry code as in Fig. 2), and are interconnected by the decavanadate anions to form a three-dimensional network (Fig. 3).

Table 2 lists the remaining hydrogen-bond distances involving solvent water molecules with O···O less than 3.1 Å.

Experimental

Commercially available reagent grade KVO$_3$ (Aldrich), NaCl (Junsei) and HNO$_3$ (Junsei) were used. Compound (I) was crystallized by mixing hot aqueous solutions of KVO$_3$ (2.0 g in 40 ml) and NaCl (1.7 g in 20 ml), and adjusting the pH to about 6.8 by adding a 3*M* HNO$_3$ solution dropwise while vigorously stirring. The solution was concentrated to about 20 ml in a water bath. After 1 d, pale-brown crystals of pseudo-hexagonal habit were isolated at room temperature. Thermogravimetric analysis, carried out in a flow of air, showed a weight loss of 8.51% in a single broad step between 315 and 573 K.

Crystal data

Na$_4$K$_2$[V$_{10}$O$_{28}$]·18H$_2$O	$Z = 4$
$M_r = 1451.85$	$D_x = 2.391$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.738$ (2) Å	$\mu = 2.59$ mm^{-1}
$b = 12.636$ (1) Å	$T = 298$ (2) K
$c = 20.042$ (5) Å	Hexagonal prism, pale brown
$\beta = 116.114$ (9)°	$0.68 \times 0.62 \times 0.53$ mm
$V = 4033.6$ (11) Å^3	

Data collection

Stoe Stadi-4 diffractometer	4595 independent reflections
$\omega/2\theta$ scans	3143 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$\theta_{max} = 27.5°$
(*X-SHAPE*; Stoe & Cie, 1996)	3 standard reflections
$T_{min} = 0.192$, $T_{max} = 0.234$	frequency: 60 min
4595 measured reflections	intensity decay: 3.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 29.2336P]$
$wR(F^2) = 0.124$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
4595 reflections	$\Delta\rho_{max} = 0.62$ e Å^{-3}
288 parameters	$\Delta\rho_{min} = -0.55$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: *SHELXL97* (Sheldrick, 1997)
	Extinction coefficient: 0.00091 (5)

Table 1
Selected bond lengths (Å).

V1···V2	3.078 (1)	V4—O*B*6	1.809 (3)
V1···V3^i	3.083 (1)	V4—O*B*7	1.862 (3)
V1···V4	3.169 (1)	V4—O*T*13	1.610 (3)
V1···V5	3.150 (1)	V5—O*H*1	2.236 (3)
V2···V3	3.090 (1)	V5—O*C*2^i	1.994 (3)
V2···V4	3.116 (1)	V5—O*C*3	2.009 (3)
V2···V5	3.122 (1)	V5—O*B*8	1.839 (3)
V3···V4	3.123 (1)	V5—O*B*9	1.818 (3)
V3···V5	3.124 (1)	V5—O*T*14	1.617 (3)
V4···V5^i	3.060 (1)	K—O*W*3	2.882 (4)
V1—O*H*1	2.123 (3)	K—O*W*4	2.885 (5)
V1—O*H*1^i	2.125 (3)	K—O*T*13^i	2.931 (4)
V1—O*C*2	1.958 (3)	K—O*T*11^{ii}	2.947 (4)
V1—O*C*3	1.892 (3)	K—O*T*12^{iii}	2.990 (4)
V1—O*B*4	1.692 (3)	K—O*W*1	3.028 (6)
V1—O*B*10	1.699 (3)	K—O*W*2	3.079 (6)
V2—O*H*1	2.331 (3)	K—O*T*14	2.933 (4)
V2—O*B*4	2.034 (3)	K—O*C*3	3.111 (3)
V2—O*B*5	1.839 (3)	Na1—O*W*3	2.387 (4)
V2—O*B*6	1.891 (3)	Na1—O*W*2	2.383 (6)
V2—O*B*8	1.865 (3)	Na1—O*W*7	2.399 (4)
V2—O*T*11	1.607 (3)	Na1—O*W*4	2.399 (4)
V3—O*H*1	2.324 (3)	Na1—O*W*5	2.400 (4)
V3—O*B*5	1.843 (3)	Na1—O*W*6	2.419 (5)
V3—O*B*7	1.853 (3)	Na2—O*W*7	2.370 (4)
V3—O*B*9	1.901 (3)	Na2—O*W*8	2.402 (4)
V3—O*B*10^i	2.049 (3)	Na2—O*B*10	2.497 (4)
V3—O*T*12	1.614 (3)	Na3—O*W*1^{iv}	2.338 (5)
V4—O*H*1	2.233 (3)	Na3—O*W*8	2.389 (4)
V4—O*C*2	1.975 (3)	Na3—O*T*12^v	2.456 (3)
V4—O*C*3^i	2.025 (3)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O*W*1—H*W*1*A*···O*W*5^{vi}	0.97	2.07	2.989 (7)	157
O*W*1—H*W*1*B*···O*W*9^{ii}	0.97	2.33	3.082 (7)	134
O*W*2—H*W*2*B*···O*B*7^{iii}	0.82 (7)	2.04 (7)	2.842 (5)	165 (7)
O*W*2—H*W*2*A*···O*B*7^i	0.77 (7)	2.13 (7)	2.892 (5)	171 (7)
O*W*3—H*W*3*A*···O*B*5^{iii}	0.97	1.90	2.826 (5)	158
O*W*3—H*W*3*B*···O*B*5^{ii}	0.97	1.92	2.864 (5)	163
O*W*4—H*W*4*A*···O*B*8^{ii}	0.97	1.93	2.820 (5)	151
O*W*4—H*W*4*B*···O*B*8	0.97	2.24	2.956 (5)	130
O*W*5—H*W*5*B*···O*B*9^{ii}	0.96	1.95	2.847 (5)	154
O*W*5—H*W*5*A*···O*T*13^{vii}	0.96	2.18	2.941 (5)	136
O*W*6—H*W*6*B*···O*B*6^{iii}	0.97	2.16	2.871 (5)	130
O*W*6—H*W*6*A*···O*T*14^v	0.95	2.58	2.908 (5)	101
O*W*7—H*W*7*A*···O*C*2^{vii}	0.97	1.90	2.838 (5)	161
O*W*7—H*W*7*B*···O*W*9	0.97	1.97	2.889 (7)	158
O*W*8—H*W*8*B*···O*B*9^i	0.97	2.08	2.903 (5)	142

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

A first data collection from a smaller crystal (0.44 × 0.25 × 0.25 mm) revealed a monoclinic cell with $a = 17.737$ (3), $b = 12.635$ (2) and $c = 10.019$ (2) Å, and $\beta = 116.11$ (1)°. Refinement in space group $C2/m$ converged with similar R values, but some of the atoms were disordered. A second data collection using a larger crystal (this study) gave the correct space group ($C2/c$) with a doubling of the c axis compared with the first measurement. The H atoms of the water molecules were included in the final cycles of refinement in a riding model, with O—H distances ranging from 0.77 to 0.97 Å and O—H···O angles ranging from 100.8 to 171 (7)°. The H atoms of the O*W*9 water molecule could not be positioned geometrically or located in an electron-density map. They were therefore excluded from the refinement.

Data collection: *STADI4* (Stoe & Cie, 1996); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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