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Potassium–sodium double salt of decavanadate, $K_4Na_2[V_{10}O_{28}]\cdot 10H_2O$

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The double salt tetrapotassium disodium decavanadate decahydrate, $K_4Na_2[V_{10}O_{28}]\cdot 10H_2O$, crystallizes in the triclinic system in space group $P\overline{1}$. The centrosymmetric $[V_{10}O_{28}]^{6-}$ polyanion forms a three-dimensional network *via* $O_{polyanion}\cdots K^+\cdots O_{polyanion}$ coordination with K^+ ions and $O_{polyanion}\cdots H—O_{water}\cdots Na^+$ hydrogen bonds. The V$\cdots$V distances are in the range 3.0601 (9)–3.271 (1) Å, and the four types of V—O bond lengths are in the ranges 1.597 (2)–1.621 (2) (O*t*), 1.920 (2)–2.020 (2) (O*c*), 1.682 (2)–2.072 (2) (O*b*) and 2.088 (2)–2.368 (2) Å (O*h*).

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(V–O) = 0.002 Å
R factor = 0.034
wR factor = 0.094
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Simple decavanadate salts of alkali metals or ammonium have been reported, *viz*. $Na_6[V_{10}O_{28}]\cdot 18H_2O$ (Durif *et al.*, 1980), $Na_6[V_{10}O_{28}]\cdot 12H_2O$ (Xu *et al.*, 1996), $Na_2[H_4V_{10}O_{28}]\cdot 14H_2O$

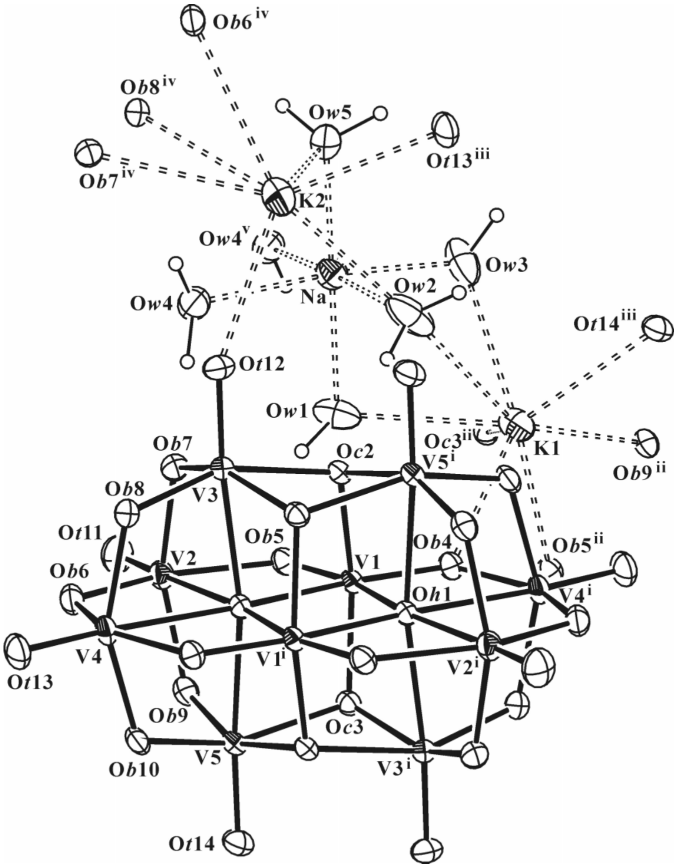

Figure 1
A view of the title structure with 50% probability displacement ellipsoids, showing the full coordination of the cations. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $x-1, 1+y, z$; (iv) $1-x, 1-y, 2-z$; (v) $-x, 1-y, 2-z$.]

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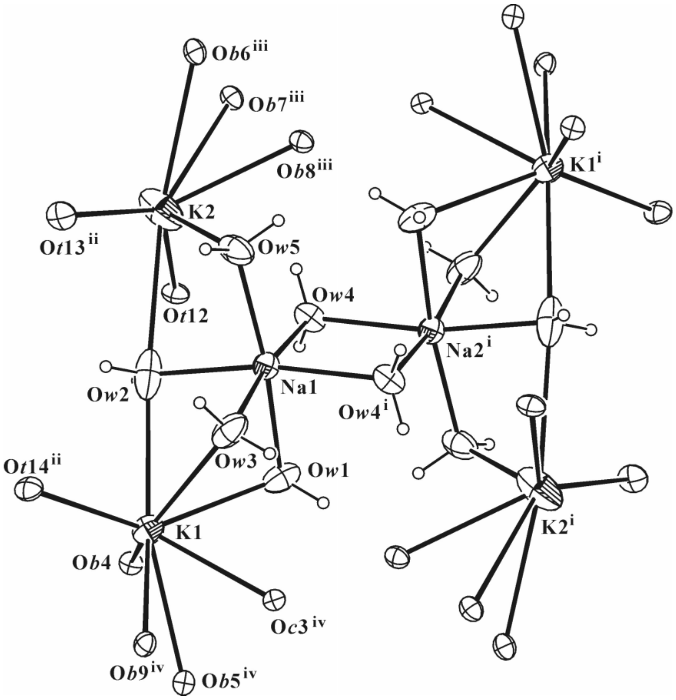

Figure 2
The coordination of K^+ and Na^+ ions in (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $x-1, 1+y, z$; (iii) $1-x, 1-y, 2-z$; (iv) $-x, 1-y, 1-z$; (v) $x, 1-y, 2-z$.]

(Zhang *et al.*, 1985), $Na_3[H_3V_{10}O_{28}]\cdot 15H_2O$ (Duraisamy *et al.*, 2000), $K_6[V_{10}O_{28}]\cdot 9H_2O$ (Xu *et al.*, 1997), $Cs_4[H_2V_{10}O_{28}]\cdot 4H_2O$ (Rigotti *et al.*, 1987) and $(NH_4)_6[V_{10}O_{28}]\cdot 6H_2O$ (Eglmeier *et al.*, 1993), and double salts of alkali metal with ammonium, *viz.* $(NH_4)_4Na_2[V_{10}O_{28}]\cdot 10H_2O$ (Fratzky *et al.*, 2000). However, no alkali metal double salt has yet been reported.

Although the ideal symmetry of the decavanadate anion is D_{2h} (mmm), all the decavanadates that have been reported show only C_1 (1) or C_i ($\bar{1}$) symmetry. The preparation of decavanadates that have higher symmetry in the solid state is a crystallographically interesting and significant challenge. The title compound, tetrapotassium disodium decavanadate decahydrate, $K_4Na_2[V_{10}O_{28}]\cdot 10H_2O$, (I), was obtained as a result of an attempt to prepare a high-symmetry decavanadate anion. We plan, in the future, to report the two double salt decavanadates, $K_4Na[HV_{10}O_{28}]\cdot 10H_2O$ and $K_2Na_4[V_{10}O_{28}]\cdot 18H_2O$ which have space groups $P2/n$ and $C2/m$, respectively.

Fig. 1 shows the structure of (I) and the labeling scheme of the decavanadate anion. The centrosymmetric polyanion consists of five independent $[VO_6]$ octahedra, sharing edges, and has C_i ($\bar{1}$) symmetry. The labeling of the O atoms in the polyanion is the same as the labeling in the previously reported structure (Lee *et al.*, 2003). The $V\cdots V$ distances are in the range 3.0601 (9)–3.271 (1) Å; the V—O distances given in Table 1 are normal. The bond lengths and angles of the $[V_{10}O_{28}]^{6-}$ anion show a similar trend to those found in the literature. The framework of $[V_{10}O_{28}]^{6-}$ has been studied in detail previously (Evans, 1966; Nowogrocki *et al.*, 1997).

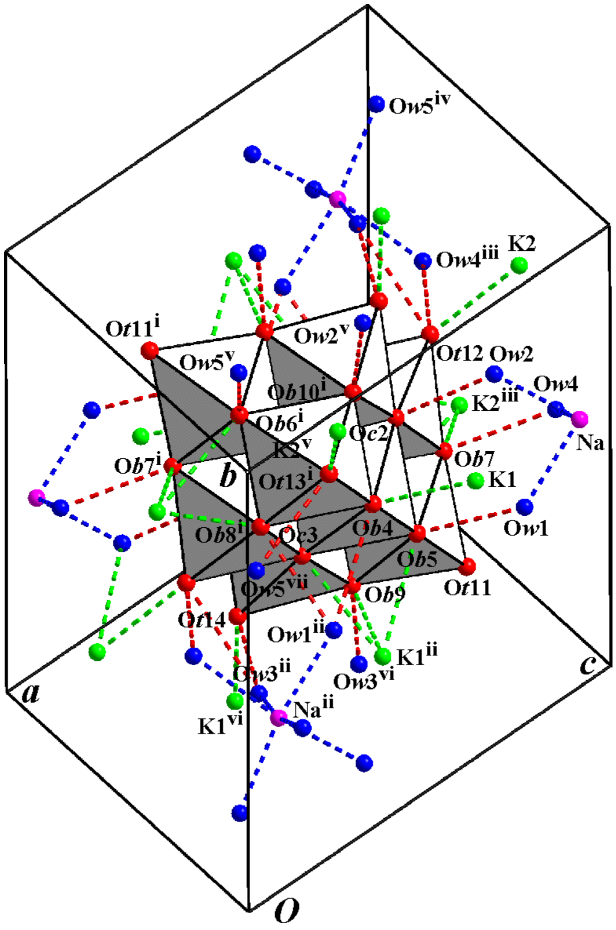

Figure 3
The unit-cell packing and interactions of O atoms in the polyanion of (I). Probable $O_{poyanion}\cdots H—O_w$ hydrogen-bonds are shown in red broken lines. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 2-z$; (iv) $1+x, y, z$; (v) $-x, 2-y, 1-z$ (vi) $1+x, y-1, z$; (vii) $x, y, z-1$.]

Fig. 2 shows the discrete cluster of Na, K1 and K2 coordinated by O atoms. The decavanadate anion is surrounded by these clusters. The K1 and K2 ions are coordinated by eight and seven O atoms, $[K1(Ob)_3(Ot)(Oc)(Ow)_3]^+$ and $[K2(Ob)_3(Ot)_2(Ow)_2]^+$, with a distance range of 2.788 (3)–3.313 (4) Å and the Na^+ ion is coordinated by six waters of crystallization, with a distance range of 2.325 (3)–2.444 (3) Å.

Fig. 3 shows the unit cell packing with $K^+\cdots O_{polyanion}$, the coordination features of Na^+ ions, and $O_{poyanion}\cdots H—Ow$ hydrogen bonding in (I). All of the surface O atoms of the decavanadate anion are coordinated to the K^+ ion, except the atoms O*c*2, O*b*10 and O*t*11. The Na^+ ion is coordinated only by water of crystallization.

All the water molecules of crystallization form hydrogen bonds with O atoms of the decavanadate and there are no O*w*—H$\cdots$O*w* hydrogen-bond interactions. All of the surface O atoms in the decavanadate anion form hydrogen bonds with the waters of crystallization except atoms O*c*3, O*b*7 and O*t*11. Atom O*t*11 does not form any interactions. Hydrogen-bond distances, less than 3.1 Å, formed by water molecules of crystallization are listed in Table 2.

Experimental

Compound (I) was obtained by mixing hot aqueous solutions of KVO_3 (2.0 g/30 ml) and NaCl (1.0 g/20 ml), and adjusting the pH to about 5.0. The pH was adjusted by adding 3 *M* HNO_3 dropwise while stirring vigorously. After a day, pale brown crystals of (I) were isolated at room temperature.

Crystal data

$Na_2K_4(V_{10}O_{28})\cdot 10H_2O$
$M_r = 1339.94$
Triclinic, $P\overline{1}$
$a = 8.620$ (1) Å
$b = 10.387$ (1) Å
$c = 11.017$ (2) Å
$\alpha = 69.22$ (1)°
$\beta = 87.14$ (1)°
$\gamma = 66.12$ (1)°
$V = 838.2$ (2) Å^3

$Z = 1$
$D_x = 2.654$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
$\theta = 9.5$–10.5°
$\mu = 3.30$ mm^{-1}
$T = 298$ (2) K
Hexagonal prism, pale brown
0.44 × 0.30 × 0.19 mm

Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
$T_{min} = 0.317$, $T_{max} = 0.534$
3845 measured reflections
3845 independent reflections
3393 reflections with $I > 2\sigma(I)$

$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.094$
$S = 1.11$
3845 reflections
244 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 1.8027P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.95$ e Å^{-3}
$\Delta\rho_{min} = -1.08$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

V1—O*h*1	2.088 (2)	V5—O*c*3	1.995 (2)
V1—O*h*1^{i}	2.132 (2)	V5—O*b*9	1.819 (2)
V1—O*c*2	1.924 (2)	V5—O*b*10	1.829 (2)
V1—O*c*3	1.920 (2)	V5—O*t*14	1.619 (2)
V1—O*b*4	1.682 (2)	K1—O*c*3^{ii}	2.923 (2)
V1—O*b*5	1.707 (2)	K1—O*b*4	2.807 (2)
V2—O*h*1^{i}	2.368 (2)	K1—O*b*5^{ii}	2.951 (2)
V2—O*b*5	2.019 (2)	K1—O*b*9^{ii}	2.973 (2)
V2—O*b*6	1.858 (2)	K1—O*t*14^{iii}	2.870 (2)
V2—O*b*7	1.881 (2)	K1—O*w*1	2.937 (3)
V2—O*b*9	1.885 (2)	K1—O*w*2	3.047 (4)
V2—O*t*11	1.597 (2)	K1—O*w*3	2.938 (4)
V3—O*h*1^{i}	2.228 (2)	K2—O*b*6^{iv}	3.086 (3)
V3—O*c*2	1.997 (2)	K2—O*b*7^{iv}	3.172 (2)
V3—O*c*3^{i}	2.020 (2)	K2—O*b*8^{iv}	2.966 (3)
V3—O*b*7	1.824 (2)	K2—O*t*11^{v}	3.420 (3)
V3—O*b*8	1.821 (2)	K2—O*t*12	2.827 (2)
V3—O*t*12	1.621 (2)	K2—O*t*13^{iii}	2.788 (3)
V4—O*h*1^{i}	2.291 (2)	K2—O*w*2	3.313 (4)
V4—O*b*4^{i}	2.072 (2)	K2—O*w*5	2.889 (4)
V4—O*b*6	1.822 (2)	Na—O*w*1	2.337 (3)
V4—O*b*8	1.893 (2)	Na—O*w*2	2.325 (3)
V4—O*b*10	1.864 (2)	Na—O*w*3	2.365 (3)
V4—O*t*13	1.613 (2)	Na—O*w*4	2.407 (3)
V5—O*h*1^{i}	2.253 (2)	Na—O*w*4^{vi}	2.444 (3)
V5—O*c*2^{i}	2.015 (2)	Na—O*w*5	2.324 (3)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $x-1, 1+y, z$; (iv) $1-x, 1-y, 2-z$; (v) $x, 1+y, z$; (vi) $-x, 1-y, 2-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*w*1—H*w*1*a*···O*b*4^{i}	0.97	2.64	3.100 (3)	109
O*w*1—H*w*1*b*···O*b*5	0.97	1.94	2.811 (3)	148
O*w*2—H*w*2*a*···O*c*2	0.98	1.95	2.856 (3)	152
O*w*2—H*w*2*b*···O*b*10^{ii}	0.93	1.95	2.839 (4)	160
O*w*3—H*w*3*a*···O*b*9^{ii}	0.97	1.91	2.767 (3)	146
O*w*3—H*w*3*b*···O*t*14^{i}	0.97	2.50	2.989 (4)	111
O*w*4—H*w*4*b*···O*b*7	0.97	1.83	2.799 (3)	174
O*w*4—H*w*4*a*···O*t*12^{iii}	0.97	2.28	2.980 (3)	128
O*w*5—H*w*5*b*···O*b*6^{ii}	0.97	1.84	2.789 (4)	163
O*w*5—H*w*5*a*···O*t*13^{iii}	0.97	2.37	2.959 (4)	119

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-1, 1+y, z$; (iii) $1-x, 1-y, 2-z$.

All H atoms of the waters of crystallization were placed in calculated positions or at electron-density peaks (H atoms of O*w*2), with O—H distances ranging from 0.93 to 0.98 Å and O—H···O angles ranging from 109 to 174°. They were included in the refinement in the riding-motion approximation, with $U_{iso}(H) = 1.5U_{eq}(O)$. The highest peak in the difference map is 0.80 Å from K2 and the largest hole is 0.85 Å from K2.

Data collection: *Stadi*4 (Stoe & Cie, 1996); cell refinement: *Stadi*4; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

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