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A novel monoprotonated decavanadate, $K_4Na[HV_{10}O_{28}]\cdot10H_2O$

Uk Lee* and Hea-Chung Joo

Department of Chemistry, Pukyong National University, 599-1 Daeyeon-3dong Nam-ku, Pusan 608-737, South Korea

Correspondence e-mail: uklee@mail.pknu.ac.kr

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(V–O) = 0.003 Å
H-atom completeness 0%
R factor = 0.046
wR factor = 0.128
Data-to-parameter ratio = 15.5

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

The novel monoprotonated decavanadate species $[HV_{10}O_{28}]^{5-}$ has been prepared and characterized. The title compound, tetrapotassium sodium hydrogendecavanadate decahydrate, crystallizes in the monoclinic system in space group $P2/n$, with the polyanion having twofold crystallographic symmetry. The protonated O atom in the polyanion was identified from the elongation of the V—O bond and the shortest O···O inter-polyanion distance. The H atom is disordered around a twofold axis that relates two hydrogen-bonded polyanions.

Comment

The preparation of decavanadates which have higher symmetry or novel protonated species in the solid state is a crystallographically interesting and significant challenge. Protonated alkali metal decavanadate species, *viz.* $Cs_4[H_2V_{10}O_{28}]\cdot4H_2O$ (Rigotti *et al.*, 1987), $Na_3[H_3V_{10}O_{28}]\cdot15H_2O$ (Duraisamy *et al.*, 2000) and $Na_2[H_4V_{10}O_{28}]\cdot14H_2O$ (Zhang *et al.*, 1985), have been reported. The $[H_nV_{10}O_{28}]^{(6-n)}$ species, where n = 2, 3 and 4, have also been characterized

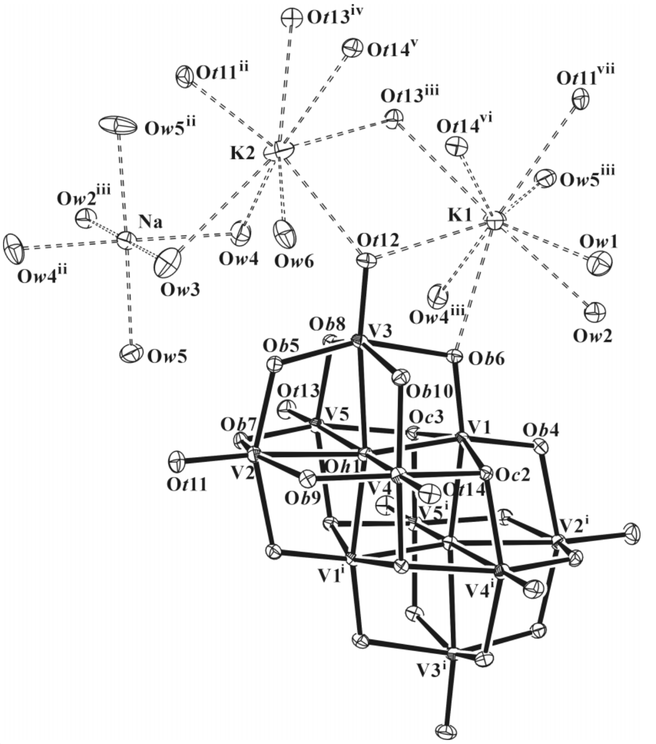

Figure 1
A view of (I) with 30% probability displacement ellipsoids, showing the coordination of the cations and the structure of the anion. [Symmetry codes: (i) $\frac{3}{2} - x, y, \frac{3}{2} - z$; (ii) $\frac{3}{2} - x, y, \frac{1}{2} - z$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $x - \frac{1}{2}, 2 - y, z - \frac{1}{2}$; (v) $x - \frac{1}{2}, 1 - y, z - \frac{1}{2}$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $x - 1, y, z$.]

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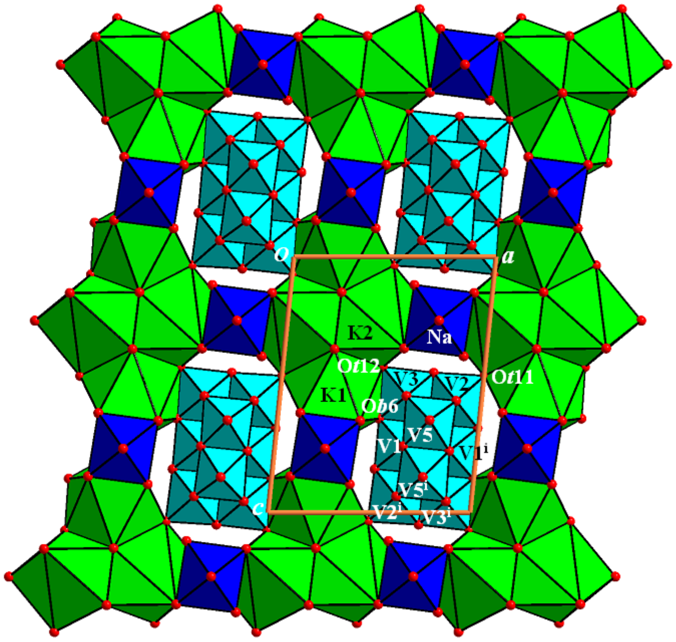

Figure 2
A polyhedral representation of the polyanions and coordinated Na, K1 and K2 ions in (I), viewed along the *b* axis [symmetry code: (i) $\frac{3}{2} - x, y, \frac{3}{2} - z$].

(Nakamura & Ozeki, 2001) as a series of tetraalkylammonium salts. Although the ideal symmetry of the decavanadate anion is D_{2h} (*mmm*), all the decavanadates that have been reported to date show only C_1 (1) or C_i ($\overline{1}$) symmetry. The monoprotonated decavanadate species, $[HV_{10}O_{28}]^{5-}$, has been characterized in solution (Baes & Mesmer, 1976) but has not yet been reported in the solid state. The title double salt, tetrapotassium sodium hydrogendecavanadate decahydrate, $K_4Na[HV_{10}O_{28}]\cdot10H_2O$, (I), was obtained as a result of an attempt to prepare a high-symmetry decavanadate anion. In the future, we plan to report the other double salt decavanadate, $K_2Na_4[V_{10}O_{28}]\cdot18H_2O$, containing a C_{2h} (2/*m*) symmetry decavanadate anion, which has space group *C*2/*m*.

Fig. 1 shows the structure of (I) and the labelling scheme for the decavanadate anion. The asymmetric unit in the polyanion consists of five independent $[VO_6]$ octahedra sharing edges, and the crystallographic twofold axis imposed by the monoclinic *P*2/*n* space group generates the other half of the polyanion. The V$\cdots$V distances are in the range 3.054 (2)–3.206 (1) Å; the V—O bond lengths are given in Table 1. The O atoms in the anion are the same terminal and bridging types as those classified in the previous report by Lee *et al.* (2003). The $[V_{10}O_{28}]^{6-}$ framework has also been studied in detail previously (Evans, 1966; Nowogrocki *et al.*, 1997).

The protonated O atom in the polyanion of (I) was identified from the elongation of the V—O bond length and the shortest inter-polyanion distance. The V3—O*b*10 and V4—O*b*10 bond lengths are 1.917 (4) and 1.908 (3) Å, respectively. These values are longer than the similar bond lengths V2—O*b*7, V5—O*b*7, V2—O*b*9 and V4—O*b*9 (mean value 1.846 Å). This tendency was also found in previously reported protonated decavanadates. The extent of the lengthening is reduced because of disorder of the H atom. The shortest inter-polyanion distance O*b*10—O*b*10($1 - x$, $1 - y$, $1 - z$) is 3.025 (7) Å. This hydrogen bond is significantly longer than in the other protonated cases because this polyanion has only one hydrogen bond, *via* the positionally disordered H atom between the two O*b*10 atoms. From these results, it can be concluded that half the O*b*10 atoms are protonated, as required by the stoichiometry.

The Na^+ ion and water molecules O*W*2 and O*W*3 lie on the twofold axis in space group *P*2/*n*. The K^+1 and K^+2 ions are coordinated by nine and eight O atoms, respectively, *viz.* [K1(O*b*)(O*t*)$_4$(O*W*)$_4$] and [K2(O*t*)$_5$(O*W*)$_3$], and the Na^+ ion is coordinated by six water molecules of crystallization.

Fig. 2 shows a representation of a polyhedral model for the two-dimensional network of the decavanadate and the K1, K2 and Na clusters coordinated by $O_{polyanion}$ or O_{water} atoms. The decavanadate anion is surrounded by K^+1, K^+2 and Na^+ ions.

Fig. 3 shows the possible hydrogen-bond interactions between the polyanions. The water molecules of crystallization are located in a way that allows them to form hydrogen-bonds. A list of possible hydrogen bonds below 3.1 Å is given in Table 1.

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 quickly adjusting the pH to about 1.7 by adding 3 *M* HNO_3 dropwise while stirring vigorously. The solution was concentrated to about 20 ml in a water bath. After 1 d, pale-brown rectangular plate crystals of (I) were isolated at room temperature.

Crystal data

$K_4Na[HV_{10}O_{28}]\cdot10H_2O$
$M_r = 1317.96$
Monoclinic, *P*2/*n*
$a = 10.804$ (2) Å
$b = 11.034$ (2) Å
$c = 13.748$ (3) Å
$\beta = 95.78$ (2)°
$V = 1630.6$ (6) Å^3
$Z = 2$
$D_x = 2.684$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 25 reflections
$\theta = 9.5$–10.4°
$\mu = 3.38$ mm^{-1}
$T = 298$ (2) K
Rectangular plate, pale brown
0.58 × 0.48 × 0.07 mm

Data collection

Stoe STADI4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
$T_{min} = 0.162$, $T_{max} = 0.772$
3731 measured reflections
3731 independent reflections
2768 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 3.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.128$
$S = 1.15$
3731 reflections
241 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 4.4779P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}

Table 1
Selected bond lengths and possible hydrogen-bond distances (Å).

V1—O*h*1	2.085 (3)	K1—O*W*1	2.808 (5)
V1—O*h*1^{i}	2.129 (3)	K1—O*W*2	2.962 (1)
V1—O*c*2	1.939 (3)	K1—O*W*4^{iii}	3.167 (5)
V1—O*c*3	1.929 (3)	K1—O*W*5^{iii}	3.073 (6)
V1—O*b*4	1.691 (3)	K2—O*t*11^{v}	2.925 (4)
V1—O*b*6	1.684 (3)	K2—O*t*12	2.773 (4)
V2—O*h*1	2.343 (3)	K2—O*t*13^{iii}	3.374 (4)
V2—O*b*4^{i}	2.036 (3)	K2—O*t*13^{vi}	2.906 (4)
V2—O*b*5	1.827 (3)	K2—O*t*14^{vii}	3.032 (4)
V2—O*b*7	1.884 (4)	K2—O*W*3	3.114 (2)
V2—O*b*9	1.881 (4)	K2—O*W*4	3.105 (5)
V2—O*t*11	1.607 (3)	K2—O*W*6	2.858 (5)
V3—O*h*1	2.292 (3)	Na—O*W*2^{iii}	2.390 (6)
V3—O*b*5	1.832 (3)	Na—O*W*3	2.348 (7)
V3—O*b*6	2.051 (3)	Na—O*W*4^{v}	2.387 (4)
V3—O*b*8	1.871 (4)	Na—O*W*4	2.387 (4)
V3—O*b*10	1.917 (4)	Na—O*W*5^{v}	2.325 (4)
V3—O*t*12	1.603 (3)	Na—O*W*5	2.325 (4)
V4—O*h*1	2.263 (3)	O*W*1···O*W*6^{viii}	2.839 (6)
V4—O*c*2	2.021 (3)	O*W*1···O*b*9^{iv}	2.845 (5)
V4—O*c*2^{i}	1.964 (3)	O*W*1···O*W*6^{iv}	2.864 (7)
V4—O*b*9	1.790 (3)	O*W*2···O*b*4^{ix}	2.938 (3)
V4—O*b*10	1.908 (3)	O*W*2···O*W*1^{ix}	3.057 (6)
V4—O*t*14	1.608 (4)	O*W*3···O*b*5	2.911 (4)
V5—O*h*1	2.273 (3)	O*W*3···O*b*5^{v}	2.911 (4)
V5—O*c*3	1.997 (3)	O*W*3···O*W*6	3.069 (7)
V5—O*c*3^{i}	1.996 (3)	O*W*3···O*W*6^{v}	3.069 (7)
V5—O*b*7	1.827 (3)	O*W*4—O*c*3^{iii}	2.919 (5)
V5—O*b*8	1.814 (3)	O*W*4···O*b*8	2.827 (5)
V5—O*t*13	1.612 (4)	O*W*4···O*b*8^{iii}	3.068 (5)
K1—O*b*6	2.838 (3)	O*W*5···O*b*7	2.796 (5)
K1—O*t*11^{ii}	2.970 (4)	O*W*5···O*b*7^{x}	2.771 (5)
K1—O*t*12	3.048 (4)	O*W*6···O*c*2^{iv}	2.738 (5)
K1—O*t*13^{iii}	2.901 (4)	O*b*10···O*b*10^{iv}	3.025 (7)
K1—O*t*14^{iv}	2.932 (4)		

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

H atoms were not located. The H atoms on O*W*2, O*W*3 and O*W*4 could not be positioned geometrically or located in an electron density map because they are coordinated to two K^+ and one Na^+. Reasonable H-atom positions for O*W*1 and O*W*6 could also not be determined, because electron-density peaks in this region gave short *D*—H···H—*D* distances of about 1.7 Å. The H atom of O*b*10—H could not be located from the electron density maps; this H atom is disordered. The highest peak in the difference map is 0.88 Å from O*W*5, and the largest hole is 0.69 Å from V3.

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

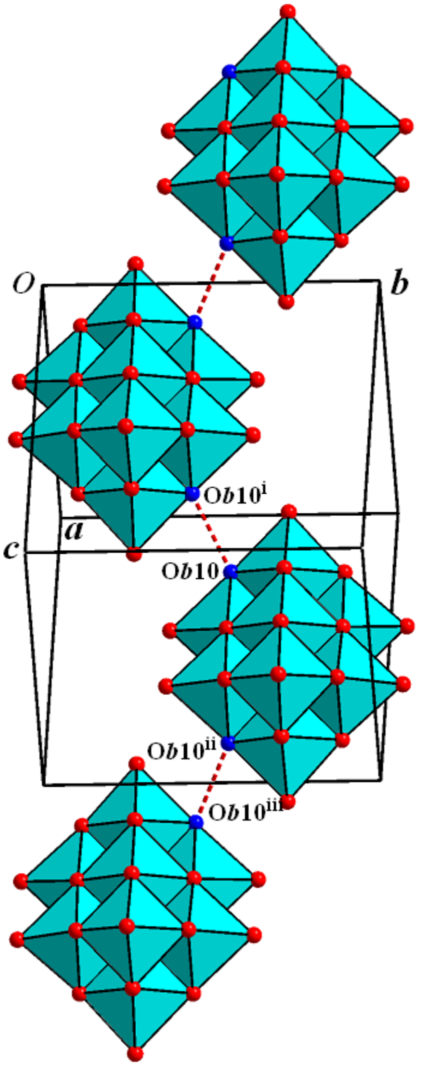

Figure 3
A possible arrangement of the interpolyanion hydrogen bond in (I). [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $\frac{3}{2}-x, y, \frac{3}{2}-z$; (iii) $\frac{1}{2}+x, 1-y, \frac{1}{2}+z$.]

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