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Tetrapotassium disodium decavanadate(V) decahydrate

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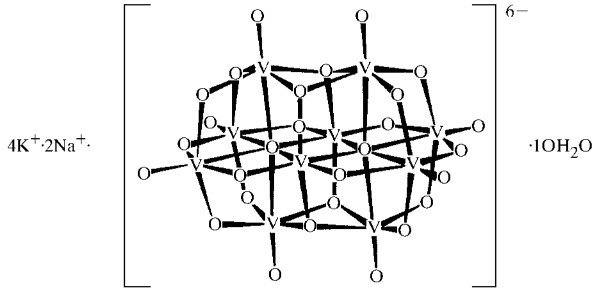
The title compound, $K_4Na_2[V_{10}O_{28}]\cdot 10H_2O$, is isostructural with the known disodium tetraammonium salt of the centrosymmetric $[V_{10}O_{18}]^{6-}$ anion.

Comment

In the course of our work with Schiff base vanadium complexes, several polyoxovanadates formed, particularly crystalline decavanadates (Cavaco *et al.*, 1995; Costa Pessoa *et al.*, 1998, 1999). In the present case, we isolated the title compound, (I), while attempting to obtain *N*-salicylidene-tyrosinate (sal–Tyr) oxovanadium complexes. The hydrolysis of vanadium(V) is very complex, but by combination of potentiometric and ^{51}V NMR spectroscopy, its speciation was determined in the whole pH range (Pettersson *et al.*, 1983). In the slightly acid pH range (3.0–5.5), yellow–orange decavanadates $[H_nV_{10}O_{28}]^{(6-n)-}$ form. The hydrolysis of vanadium(IV) is also quite complex. On increasing the pH starting in the acid range, $V^{IV}O^{2+}$ hydroxide precipitates in the pH range 4–8 (Boas & Costa Pessoa, 1987). In the present case, the pH is ~ 5, but the sal–Tyr ligand coordinates to $V^{IV}O^{2+}$ and hinders the precipitation of the hydroxide. The VO(sal–Tyr) complex is soluble, it does not precipitate and the formation of a compound of V^V may then be explained by the slow oxidation of $V^{IV}O^{2+}$ by atmospheric oxygen. Decavanadates being the dominant V^V species at pH ~ 5 therefore form slowly as crystalline compounds. This explains why several decavanadate salts have been obtained by our group under relatively similar conditions. In particular, this compound is isostructural with the disodium tetraammonium salt (Cavaco *et al.*, 1995), with the replacement of NH_4^+ by K^+ ions. Valence bond calculations show that all V—O and V═O bond distances are consistent with the non-protonation of the decavanadate ion, thus confirming the assumed overall charge of −6.



(I)

Experimental

Tyrosine was dissolved in 15 ml of an aqueous solution containing sodium acetate (2 mmol) and potassium hydroxide (2 mmol), and salicylaldehyde (4 mmol) dissolved in 18 ml of ethanol was added. 14 ml of an aqueous solution of $VOSO_4$ (4 mmol) were added slowly, followed by 1 ml of pyridine. The mixture was kept in a beaker covered with Parafilm at 277–279 K and after five weeks red–brown crystals of the title compound were separated.

Crystal data

$K_4Na_2[V_{10}O_{28}]\cdot 10H_2O$
$M_r = 1339.94$
Triclinic, $P\overline{1}$
$a = 8.5893$ (6) Å
$b = 10.3543$ (6) Å
$c = 10.9893$ (6) Å
$\alpha = 69.194$ (5)°
$\beta = 87.122$ (5)°
$\gamma = 66.172$ (5)°
$V = 830.75$ (9) Å^3

$Z = 1$
$D_x = 2.678$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.02$–15.93°
$\mu = 3.332$ mm^{-1}
$T = 293$ K
Prism, dark orange
0.40 × 0.35 × 0.30 mm

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.252$, $T_{max} = 0.368$
5134 measured reflections
4832 independent reflections
4320 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$
$\theta_{max} = 29.95$°
$h = -12 \rightarrow 0$
$k = -14 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.098$
4832 reflections
284 parameters
H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0320P)^2 + 1.1139P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 1.063$ e Å^{-3}
$\Delta\rho_{min} = -1.280$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0032 (4)

Table 1
Selected geometric parameters (Å).

V1—O15	1.6790 (14)	V2—O23	1.8140 (16)
V1—O13	1.7052 (15)	V2—O25	1.8221 (15)
V1—O7	1.9135 (14)	V2—O7	1.9903 (14)
V1—O8	1.9213 (14)	V2—O8^i	2.0076 (14)
V1—O6	2.0828 (14)	V2—O6^i	2.2475 (14)
V1—O6^i	2.1276 (13)	V2—V4	3.0708 (5)
V1—V5^i	3.0515 (5)	V2—V5	3.0878 (5)
V1—V3	3.0907 (5)	V3—O3	1.5925 (17)
V2—O2	1.6147 (16)	V3—O35	1.8525 (15)

V3—O23	1.8787 (16)	V4—O7	2.0143 (14)
V3—O34$^{\rm i}$	1.8789 (15)	V5—O5	1.6077 (16)
V3—O13	2.0144 (15)	V5—O35	1.8203 (16)
V3—O6$^{\rm i}$	2.3597 (14)	V5—O25	1.8593 (15)
V4—O4	1.6204 (15)	V5—O45$^{\rm i}$	1.8897 (15)
V4—O45	1.8146 (15)	V5—O15$^{\rm i}$	2.0670 (15)
V4—O34	1.8174 (15)	V5—O6$^{\rm i}$	2.2819 (14)
V4—O8$^{\rm i}$	1.9909 (14)		

Symmetry code: (i) $2-x, 2-y, 1-z$.

K- and Na-atom sites were assigned on the basis of the observed electron density. H atoms of water molecules were refined with their 1–2 and 1–3 distances restrained to 0.9 (2) and 1.45 (4) Å, respectively. Crystallographic software was used through the *OSCAIL* interface of McArdle (1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *SDP* (Enraf–Nonius, 1985); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick & Schneider, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick & Schneider, 1997).

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e76 Pedro M. Matias *et al.* • $K_4Na_2[V_{10}O_{28}]\cdot 10H_2O$ *Acta Cryst.* (2000). C**56**, e75–e76