

Bis[2-(2-hydroxyethyl)pyridinium] μ -decavanadato-bis[pentaaqua- manganate(II)] tetrahydrate

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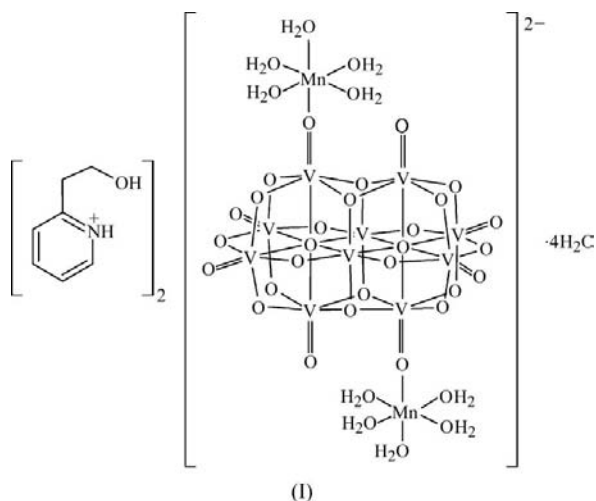
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The structure of the title compound, $(C_7H_{10}NO)_2[Mn_2V_{10}O_{28}(H_2O)_{10}] \cdot 4H_2O$ or $(C_5H_4NHCH_2CH_2OH)_2\{[Mn(H_2O)_5]_2V_{10}O_{28}\} \cdot 4H_2O$, at 293 (2) K has triclinic ($P\bar{1}$) symmetry. The asymmetric unit consists of one half of a decavanadate anion of C_i symmetry, one $[Mn(H_2O)_5]^{2+}$ group, one 2-(2-hydroxyethyl)pyridinium cation and two solvent water molecules. The decavanadate ion bridges between two $[Mn(H_2O)_5]^{2+}$ groups, thus forming a dodecanuclear complex unit. Complex units are connected *via* a hydrogen-bonding network, forming supramolecular layers lying in the (001) plane. Cations and solvent water molecules are located between these layers.

Comment

Over the past few years, the role of vanadium compounds in living organisms has been studied intensively (Rehder, 2008). The biological activity of decavanadate, for example in the modulation of ionic channels, calcium homeostasis and insulin mimetics, has been described by Aureliano & Madeira (1998).



Decavanadate ions serve as building blocks for supramolecular assemblies (da Silva *et al.*, 2003), but their role as

ligands coordinated to metal centres has only very recently been reported. As donor atoms they can serve as either terminal or bridging O atoms (Fig. 1). In the title compound, (I) (Fig. 2), the bridging doubly monodentate $[V_{10}O_{28}]^{6-}$ anion of C_i symmetry (although its symmetry is very close to the D_{2h} point group) is coordinated *via* centrosymmetrically arranged ‘out-of-the-main-plane’ [plane in the $[V_{10}O_{28}]^{6-}$ anion formed by atoms V1, V2, V3, V1^{iv}, V2^{iv} and V3^{iv}; symmetry code: (iv) $-x + 1, -y + 2, -z + 1$] terminal O1 atoms (F) to the $[Mn(H_2O)_5]^{2+}$ units, thus completing the octahedral

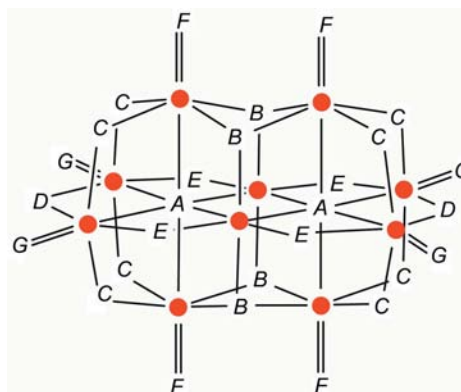


Figure 1
The scheme of the decavanadate anion with idealized D_{2h} point group geometry. A–G denote crystallographically non-equivalent O atoms and circles denote V atoms [according to da Silva *et al.* (2003)].

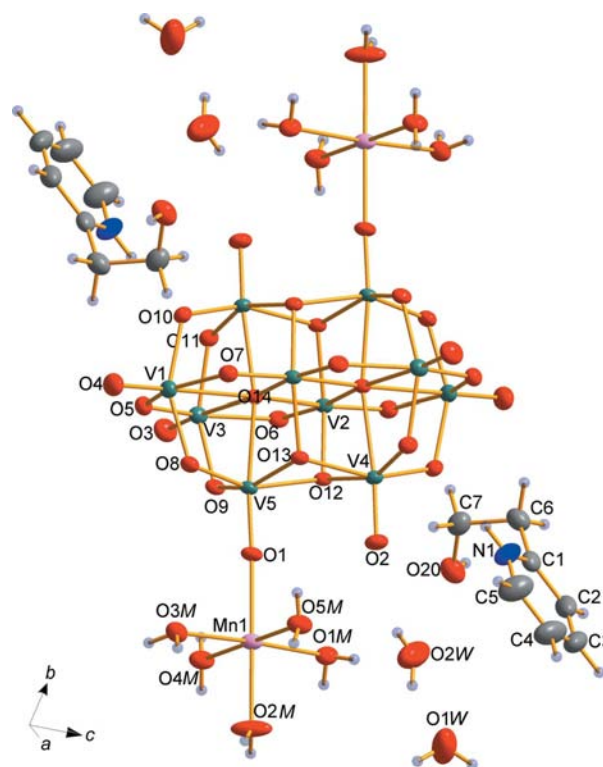


Figure 2
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The symmetry operation relating labelled atoms to unlabelled atoms is $(-x + 1, -y + 2, -z + 1)$.

coordination geometry of the Mn^{II} atoms. This is similar to the coordination of $[\text{V}_{10}\text{O}_{28}]^{6-}$ in $[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}_2(\text{H}_2\text{O})_{10}\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ (Graia *et al.*, 2008). There is also the possibility of coordination *via* 'in-the-main-plane'-lying terminal O atoms (*G*) (Klištinová *et al.*, 2008) and 'out-of-the-main-plane'-lying $\mu\text{-OV}_2$ bridging O atoms (*C*) (Li *et al.*, 2007).

The coordination possibilities of the bridging O atoms of the *B*, *D* or *E* type are evidently restricted for steric reasons.

The $\text{V5}-\text{O1}$ distance of 1.6350 (11) Å, which corresponds to the bond valence $s = 1.59$ (Brown, 1992), is slightly elongated in comparison with other $\text{V}-\text{O}_t$ (O_t is a terminal O atom) bond lengths which lie in the extremely narrow range 1.5951 (12)–1.5971 (12) Å. This distance is somewhat larger in comparison with those in $(\text{NH}_4)_2[\text{Cu}_2(\text{NH}_3\text{CH}_2\text{CH}_2\text{COO})_4(\text{V}_{10}\text{O}_{28})] \cdot 10\text{H}_2\text{O}$ ($s = 1.68$) (Klištinová *et al.*, 2008) and $[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}_2(\text{H}_2\text{O})_{10}\text{V}_{10}\text{O}_{28}] \cdot 6\text{H}_2\text{O}$ ($s = 1.63$). The averaged bond lengths of the $\text{V}-\text{O}_b$ (O_b is a bridging O atom) bonds are 1.85 (11), 1.98 (4) and 2.23 (10) Å for bridging O atoms with coordination numbers two, three and six, respectively.

The Mn^{II} atom has an octahedral coordination which is slightly shortened in the axial direction. The equatorial plane of the MnO_6 octahedron, given by atoms Mn1, O1M and O3M–O5M, is nearly parallel with the main plane of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion: the corresponding least-squares planes form an angle of 1.83 (3)°. The Mn–O distances in the equatorial plane are in the range 2.1902 (12)–2.2103 (12) Å ($s = 0.32$ –0.34). The Mn1–O1 distance of 2.1630 (11) Å ($s = 0.36$) involves the O atom that links to the decavanadate anion and the shortest distance is the Mn1–O2 bond *trans* to this [Mn1–O2M = 2.1420 (13) Å, which corresponds to $s = 0.39$].

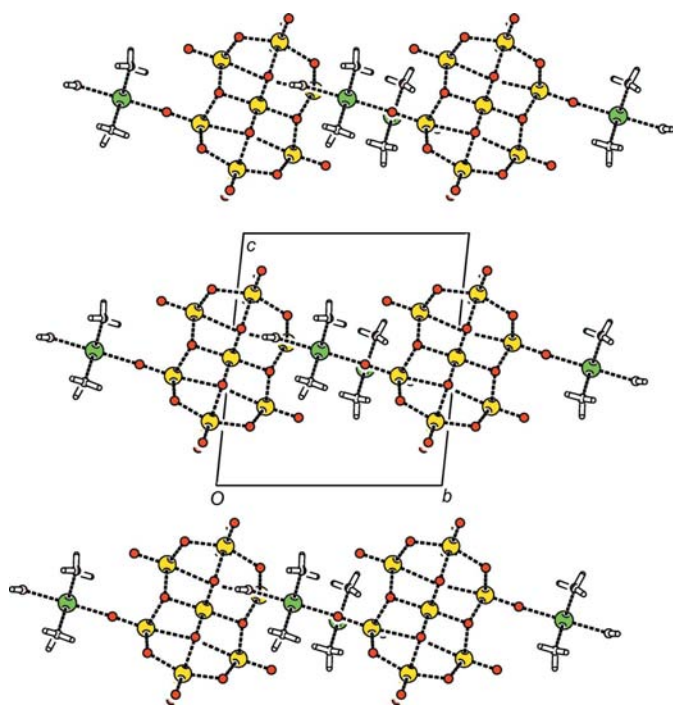


Figure 3
A view along the *a* axis of the hydrogen-bonded anionic layers.

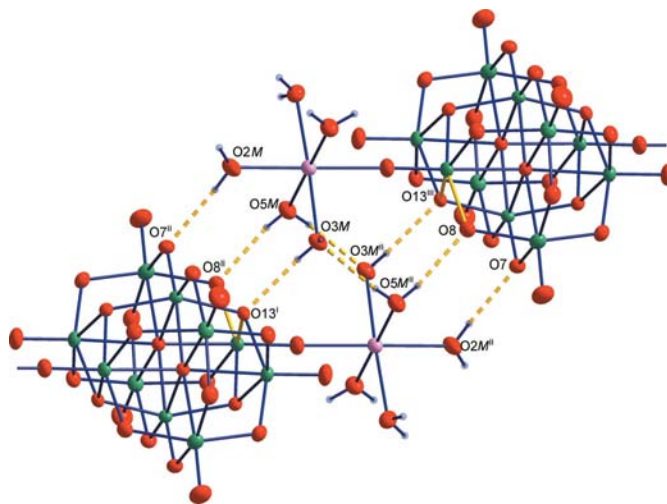


Figure 4
A detail of the $R_4^6(16)$ rings in the anionic chain. [Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$].

The dodecanuclear $[\{\text{Mn}(\text{H}_2\text{O})_5\}_2\text{V}_{10}\text{O}_{28}]^{2-}$ units are connected *via* a hydrogen-bonding network (Table 1), forming anionic supramolecular layers lying in the (001) plane (Fig. 3). In these layers, Mn-coordinated water molecules act as hydrogen-bond donors/acceptors and vanadate O atoms act as hydrogen-bond acceptors, forming interesting folded rings with graph set $R_4^6(16)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995) (Fig. 4) enforced by $\text{O2M}-\text{H21M} \cdots \text{O7}^{\text{ii}}$ and $\text{O2M}-\text{H22M} \cdots \text{O6}^{\text{i}}$ hydrogen bonds [symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$]. The negative charge of the layers is neutralized by the 2-(2-hydroxyethyl)pyridinium cations lying between these layers. Cations and solvent water molecules are also involved in the extensive hydrogen-bonding network.

To evaluate the parallel-displaced π – π interaction between the pyridine rings, neighbouring least-squares planes defined by atoms C1–C5/N1 with symmetry codes (x, y, z) and $(2 - x, 1 - y, 2 - z)$ were calculated. The interplanar distance R is 3.47 Å and the centroid–centroid distance of the aromatic rings (R_{ct}) is 4.04 Å.

Experimental

To a solution of $\text{Mn}(\text{CH}_3\text{COO})_2$ (0.346 g, 2 mmol) in water (20 ml), 2-(2-hydroxyethyl)pyridine (0.45 ml, 4 mmol) was added. The opaque solution was stirred for 15 min and an aqueous solution of NH_4VO_3 (0.468 g, 4 mmol; in 40 ml of water) was then added with the immediate formation of a precipitate. The solution with the precipitate was stirred for a further 15 min and filtered. The pH of the filtrate was adjusted to 5.0 with dilute HCl; a yellow solution was obtained, to which ethanol (10 ml) was added. Orange crystals were isolated after standing for 7 d at room temperature. The compound is stable at room temperature. The IR spectrum in KBr pellets was recorded on an FT-IR Nicolet Magna 750 spectrometer. Vanadium was determined by titration with an aqueous solution of FeSO_4 . C, H and N were estimated on a CHN analyser (Carlo Erba). The IR spectrum exhibits characteristic bands assigned to the organic cation [1640 (*m*), 1620 (*m*), 1560 (*m*), 1540 (*m*), 1505 (*m*), 1050 (*m*)] and the deca-

vanadate group [970 (*vs*), 827 (*s*), 725 (*vs*), 590 (*m*)]. Analysis calculated for $C_{14}H_{48}Mn_2N_2O_{44}V_{10}$ (found): C 10.8 (10.6), H 2.6 (3.1), N 1.8 (1.7), V 32.7% (32.2%).

Crystal data

$(C_7H_{10}NO)_2[Mn_2V_{10}O_{28}(H_2O)_{10}] \cdot 4H_2O$
 $M_r = 1567.82$
 Triclinic, $P\bar{1}$
 $a = 9.58016$ (9) Å
 $b = 11.33329$ (13) Å
 $c = 12.07540$ (17) Å
 $\alpha = 78.3429$ (11)°
 $\beta = 74.6559$ (11)°
 $\gamma = 66.0748$ (10)°
 $V = 1149.02$ (2) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 2.56$ mm⁻¹
 $T = 293$ (2) K
 0.28 × 0.25 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby (Gemini R) detector
 Absorption correction: analytical (*CrysAlisPro*; Oxford Diffraction, 2008); analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)
 $T_{min} = 0.597$, $T_{max} = 0.739$
 23048 measured reflections
 5256 independent reflections
 4821 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.056$
 $S = 1.07$
 5256 reflections
 368 parameters
 21 restraints
 H atoms treated by a mixture of constrained and restrained refinement
 $\Delta\rho_{max} = 0.35$ e Å⁻³
 $\Delta\rho_{min} = -0.35$ e Å⁻³

Table 1 Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1M—H11M...O9 ⁱ	0.810 (15)	1.850 (15)	2.6599 (16)	180 (3)
O1M—H12M...O2W	0.818 (15)	1.851 (15)	2.661 (2)	170 (2)
O2M—H21M...O7 ⁱⁱ	0.793 (15)	1.926 (15)	2.7179 (17)	177 (2)
O2M—H22M...O6 ⁱ	0.795 (15)	1.958 (15)	2.7497 (17)	174 (2)
O3M—H31M...O13 ⁱⁱ	0.779 (15)	1.952 (17)	2.7150 (15)	166 (2)
O3M—H32M...O20 ⁱ	0.827 (15)	1.833 (16)	2.6450 (18)	167 (2)
O4M—H41M...O12 ⁱ	0.797 (15)	2.023 (16)	2.8033 (15)	166 (2)
O4M—H42M...O1M ⁱ	0.809 (15)	1.970 (15)	2.7773 (18)	176 (2)
O5M—H51M...O8 ⁱⁱ	0.779 (15)	1.940 (16)	2.7113 (16)	170 (2)
O5M—H52M...O3M ⁱⁱ	0.819 (15)	2.028 (16)	2.8425 (18)	173 (2)
O1W—H11W...O11 ⁱⁱⁱ	0.826 (10)	1.991 (10)	2.812 (2)	172 (3)
O1W—H12W...O4 ⁱⁱ	0.821 (10)	2.17 (2)	2.924 (2)	152 (4)
O2W—H21W...O2	0.821 (10)	2.38 (3)	2.868 (2)	119 (3)
O2W—H21W...O5M	0.821 (10)	2.52 (3)	3.165 (3)	136 (3)
O2W—H22W...O1W	0.839 (10)	1.89 (2)	2.659 (3)	152 (4)
N1—H1...O10 ^{iv}	0.86	1.90	2.7531 (19)	175
O20—H20...O11 ^v	0.82	1.95	2.7490 (17)	166

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

H atoms of the cations were placed in geometrically idealized positions (C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å) and constrained to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C, N)$ and $1.5U_{eq}(O)$]. H atoms of the water molecules were located in a difference map and refined with interatomic O—H distances restrained to 0.82 Å and H...H to 1.324 Å to obtain reasonable geometry (Nardelli, 1999), with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *CrysAlisPro* (Oxford Diffraction, 2008); cell refinement: *CrysAlisPro*; data reduction: *CrysAlisPro*; program(s) used to solve structure: *DIRDIF2008* (Beurskens *et al.*, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008) and *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3005). Services for accessing these data are described at the back of the journal.

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