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Crystal structures of two decavanadates(V) with pentaaquamanganese(II) pendant groups: $(NMe_4)_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 5H_2O$ and $[NH_3C(CH_2OH)_3]_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 2H_2O$

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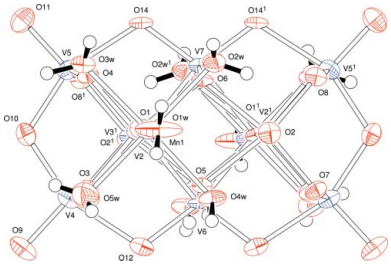
Two heterometallic decavanadate(V) compounds, bis(tetramethylammonium) decaaquadi-μ_4-oxido-tetra-μ_3-oxido-hexadeca-μ_2-oxido-hexaoxidodimanganese(II)decavanadate(V) pentahydrate, $(Me_4N)_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 5H_2O$, **A**, and bis{[tris(hydroxymethyl)methyl]ammonium} decaaquadi-μ_4-oxido-tetra-μ_3-oxido-hexadeca-μ_2-oxido-hexaoxidodimanganese(II)decavanadate(V) dihydrate, $[NH_3C(CH_2OH)_3]_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 2H_2O$, **B**, have been synthesized under mild reaction conditions in an aqueous medium. Both polyanions present two $[Mn(OH_2)_5]^{2+}$ complex units bound to the decavanadate cluster through oxide bridges. In **A**, the decavanadate unit has 2/*m* symmetry, whereas in **B** it has twofold symmetry. Apart from this, the main differences between **A** and **B** rest on the organic cations, tetramethylammonium and [tris(hydroxymethyl)methyl]ammonium, respectively, and on the number and arrangement of the water molecules of crystallization. In both compounds, the H atoms from the coordinating water molecules participate in extensive three-dimensional hydrogen-bonding networks, which link the cluster units both directly and through solvent molecules and, in **B**, through the 'tris' cation hydroxyl groups. The cation in **B** also participates in N—H···O hydrogen bonds. A number of C—H···O interactions are also observed in both structures.

1. Chemical context

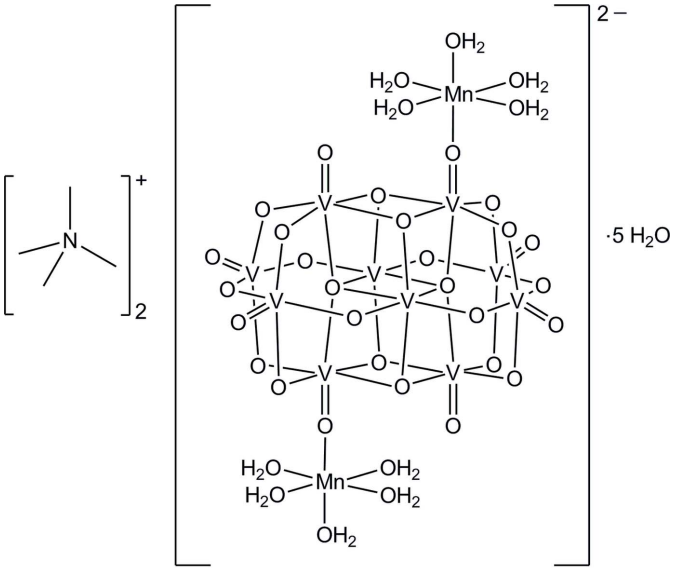
Research on the electronic properties, catalytic activities and biological roles of polyoxidovanadates has advanced enormously during the last few decades (Bošnjaković-Pavlović *et al.*, 2009; Liu & Zhou, 2010). Among these aggregates, the decavanadate(V) anion is the most intensively studied because of its biological effect on the activities of several enzymes (Aureliano & Ohlin, 2014) and its insulin-mimetic action (Chatkon *et al.*, 2013; Aureliano, 2014). The first functionalization of decavanadate anions, $[H_nV_{10}O_{28}]^{(6-n)-}$, with transition metal complexes was reported in 2007 (Li *et al.*, 2007). Since then, structures involving different binding modes with non-equivalent terminal and bridging oxido ligands have been described (Wang, Sun *et al.*, 2008; Wang, Yan *et al.*, 2008; Wang *et al.*, 2011; Long *et al.*, 2010; Xu *et al.*, 2012) and examples with first-row, *d*-block metal ions include complexation with copper(II), manganese(II) and zinc(II) (Wang, Sun *et al.*, 2008; Wang *et al.*, 2011; Klištincová *et al.*, 2009, 2010; Pavliuk *et al.*, 2014).

Polyoxidovanadates containing manganese cations have been synthesized as ionic pairs (Shan & Huang, 1999; Lin *et*



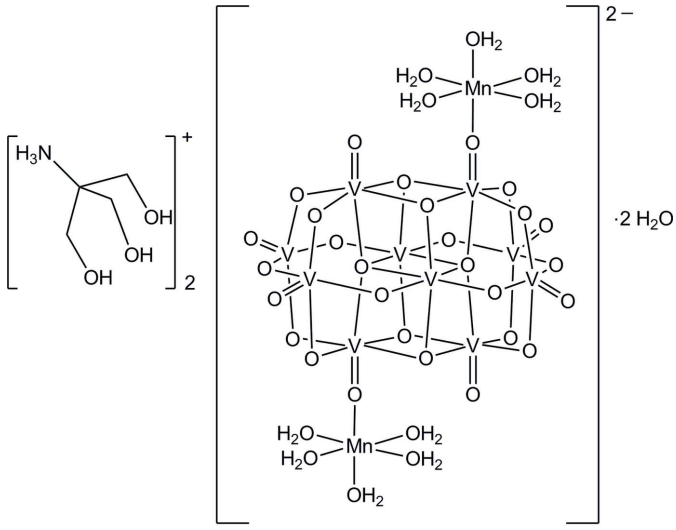
al., 2011) or as heterometallic aggregates in which the oxidovanadate cluster acts as a metalloligand to the manganese complex (Inami *et al.*, 2009; Klištincová *et al.*, 2009). Recent interest in this kind of compound lies in a possible synergistic effect (involving the two metal elements) for the enhancement of the catalytic activity towards oxidation of organic substrates, such as in the photocatalytic degradation of dyes (Wu *et al.*, 2012).

While the synthesis of decavanadates with different organic cations as building blocks for supramolecular assemblies is largely explored (da Silva *et al.*, 2003), a systematic procedure for their functionalization with transition metal complexes has not been well established. Our research group is currently involved in the synthesis of heterometallic polyoxidovanadates containing manganese(II) because of their potential activity as catalysts of olefin epoxidation. In this context, the reaction between NH_4VO_3 and mannitol to give **A** was carried out in aqueous solution in the presence of tetramethylammonium chloride (molar proportion 2:1:2), following a procedure described earlier by our group to produce the mixed-valence polyoxidovanadate $(Me_4N)_6[V_{15}O_{36}(Cl)]$ (Nunes *et al.*, 2012). The dark-green solution obtained after reflux for 24 h received one molar equivalent of $Mn(OAc)_2{\cdot}4H_2O$ and was kept under reflux for 24 more hours. A mixture of dark-green crystals of $(Me_4N)_6[V_{15}O_{36}(Cl)]$ and yellow prisms of $(NMe_4)_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]{\cdot}5H_2O$ (**A**) was isolated after four weeks at room temperature, the latter in 9% yield. Product **A** contains two tetramethylammonium cations and the $[V_{10}O_{28}]^{6-}$ unit is covalently bound to two $[Mn(OH_2)_5]^{2+}$ complexes by terminal oxido bridges.



Compound **A**

The rational synthesis of the heteropolyanion $[V_{10}O_{28}\{Mn(H_2O)_5\}_2]^{2-}$, in its turn, was achieved by reaction of NH_4VO_3 with tris(hydroxymethyl)methylamine ('tris') and manganese(II) chloride at pH 3 in a 5:3:1 molar proportion. Yellow crystals of $[NH_3C(CH_2OH)_3]_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]{\cdot}2H_2O$ (**B**) were isolated in 12% yield, as the only reaction product, after one week at room temperature. X-ray diffraction analyses revealed very similar structures for the heteropolyanions in **A** and **B**.



Compound **B**

2. Structural commentary

The anionic heteropolyanions are essentially identical in the two complexes. However, in **A**, the molecule lies about the centre of the cell which is a point of 2/*m* symmetry, so that the unique part of the anionic cluster is one quarter of that heteropolyanion. The anion lies about a mirror plane which

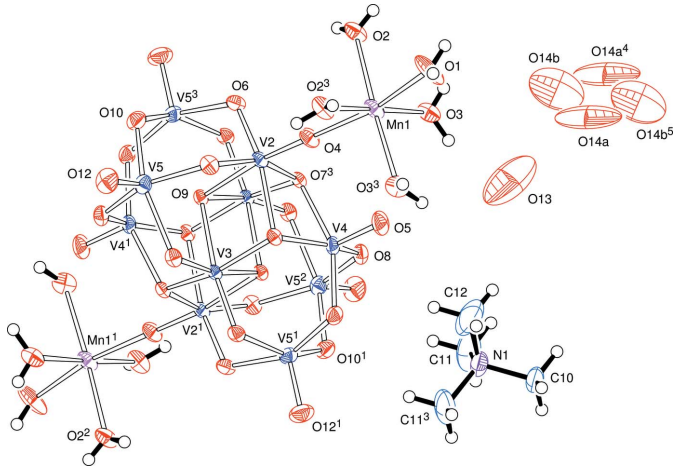


Figure 1
View of the components of $(NMe_4)_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]{\cdot}5H_2O$, **A**, indicating the atom-numbering scheme. No H atoms were identified on the disordered solvent water molecules. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (1) $1-x, y, 1-z$; (2) $1-x, 1-y, 1-z$; (3) $x, 1-y, z$; (4) $1-x, -y, -z$; (5) $1-x, y, -z$.]

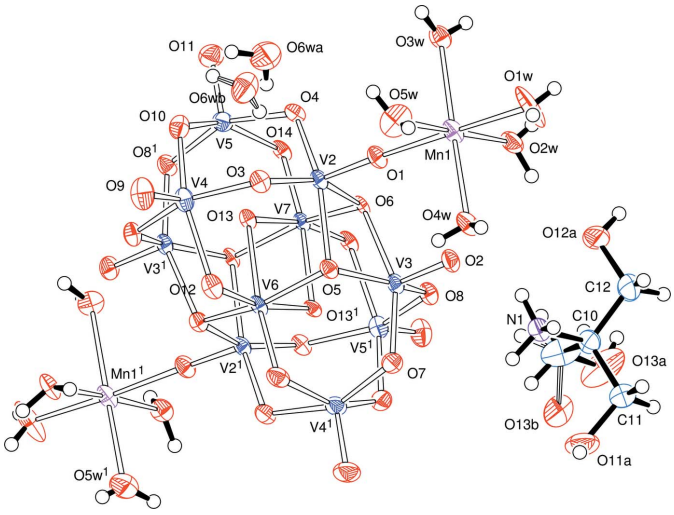


Figure 2
The corresponding view for $[NH_3C(CH_2OH)_3]_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 2H_2O$, **B**. [Symmetry code: (1) $1-x, y, \frac{1}{2}-z$.]

passes through the V2, V4 and manganese atoms, and there is a twofold symmetry axis which is perpendicular to the mirror plane and passes through V3 and the centre of the cell, Fig. 1.

The $V_{10}O_{28}$ moiety in the structure of compound **B** lies about a twofold symmetry axis which passes through the vanadium atoms V6 and V7, Fig. 2. This is the only crystallographic symmetry in this ion which, nevertheless, shows a very similar structure to that found in the ion in compound **A**;

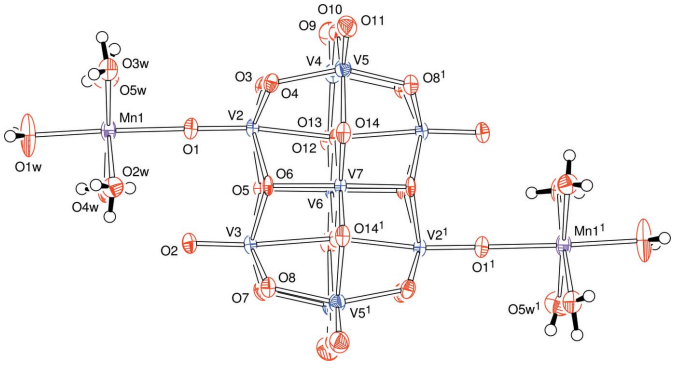


Figure 3
The anion of compound **B** viewed approximately down the *a* axis of the $V_{10}O_{28}$ moiety. [Symmetry code: (1) $1-x, y, \frac{1}{2}-z$.]

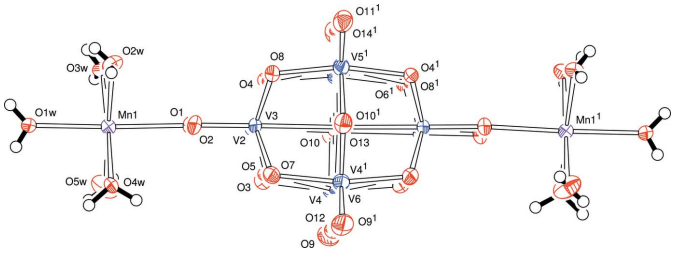


Figure 4
The anion of compound **B** viewed approximately down the *b* axis of the $V_{10}O_{28}$ moiety. [Symmetry code: (1) $1-x, y, \frac{1}{2}-z$.]

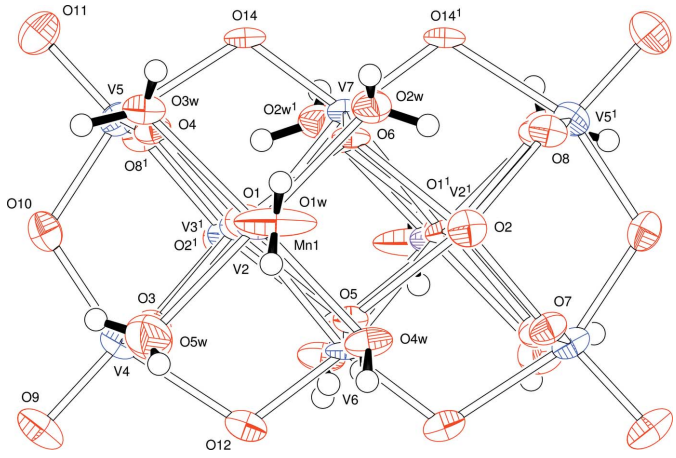


Figure 5
The anion of compound **B** viewed approximately down the *c* axis of the $V_{10}O_{28}$ moiety. [Symmetry code: (1) $1-x, y, \frac{1}{2}-z$.]

views showing this pseudo-symmetry are presented in Figs. 3, 4 and 5. The unique part here is one half of the anion. The previously reported analysis of this anion [with a 2-(2-hydroxyethyl)pyridinium cation] showed the cluster to be lying about an inversion centre (Klištincová *et al.*, 2009).

Bond angles and lengths determined for $[V_{10}O_{28}\{Mn(H_2O)_5\}_2]^{2-}$ are in the ranges reported in the literature (Klištincová *et al.*, 2009). In both our compounds, there is a wide range of V—O bond lengths. The vanadium atoms on the outer shell of the heteropolyanions, *e.g.* V4 and V5 in **A**, and V2–V5 in **B**, are five-coordinate with a square-pyramidal pattern; there is a sixth oxygen atom in the direction of an octahedral site but, at *ca* 2.3 Å from the vanadium atom, rather longer than the normal coordination distance. Of the five bonded oxygen atoms, the apical site (opposite the distant, sixth, site) has the shortest V—O distance, *ca* 1.6 Å, corresponding to a vanadyl group. The more 'internal' vanadium atoms in each structure, *viz* V3 in **A**, and V6 and V7 in **B**, have more uniform V—O distances in more regular octahedral patterns.

Table 1
Hydrogen-bond geometry (Å, °) for compound **A**.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O11^{i}	0.76 (2)	1.97 (2)	2.7199 (14)	168 (2)
O2—H2A···O7^{i}	0.72 (2)	2.04 (2)	2.7457 (15)	167 (2)
O2—H2B···O3^{ii}	0.78 (2)	2.05 (2)	2.8295 (18)	178 (2)
O3—H3A···O6^{ii}	0.74 (3)	1.92 (3)	2.6573 (16)	174 (3)
O3—H3B···O13	0.87 (3)	1.91 (3)	2.737 (3)	158 (3)
C10—H10A···O11^{iii}	0.96	2.51	3.362 (2)	148
C10—H10B···O11^{iv}	0.96	2.51	3.362 (2)	148
C10—H10C···O2^{v}	0.96	2.58	3.370 (3)	139
C10—H10C···O2^{vi}	0.96	2.57	3.370 (3)	141
C11—H11A···O8^{vii}	0.96	2.48	3.384 (3)	156
C12—H12A···O12^{iii}	0.96	2.60	3.474 (4)	152
C12—H12C···O12^{iv}	0.96	2.59	3.474 (4)	153

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

3. Supramolecular features

In both compounds, O—H···O hydrogen bonds from all the coordinating water molecules link the anions with neighbouring anions, either directly, through both the cluster O atoms and the coordinating water molecules, or indirectly through the solvent water molecules (Tables 1 and 2). In compound **B**, additional hydroxyl groups are available in the 'tris' cation, and these add further links in the extensive hydrogen bonding scheme. Additional C—H···O interactions are observed in the structures of both compounds.

4. Database survey

For structures with the $[V_{10}O_{28}\{Mn(H_2O)_5\}_2]^{2-}$ heteropolyanion, see: Klištincová *et al.* (2009). For structures with manganese(II) coordination complexes as counter-ions for $[V_{10}O_{28}]^{6-}$, see: Klištincová *et al.* (2010); Shan & Huang (1999); Lin *et al.* (2011) and Mestiri *et al.* (2013).

5. Synthesis and crystallization

General

All reactions were performed in air with purified (Milli-Q®) water. Commercial reagents were used without purification. The starting materials NH_4VO_3, $MnCl_2{\cdot}4H_2O$ and $Mn(OAc)_2{\cdot}4H_2O$ were supplied by Aldrich, while mannitol $[C_6H_8(OH)_6]$ and $(Me_4N)Cl$ were purchased from USB and Merck, respectively. Infrared (FTIR) spectra were recorded on a BIORAD FTS-3500GX spectrophotometer from KBr pellets in the 400–4000 cm^{-1} region.

Synthesis of $(NMe_4)_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]{\cdot}5H_2O$ (A)

Solid NH_4VO_3 (0.500 g, 4.27 mmol) and $[(CH_3)_4N]Cl$ (0.468 g, 4.27 mmol) were added to a solution of mannitol (0.366 g, 2.13 mmol) in 60 mL of water to produce a suspension that turned into a deep blue–greenish solution after one hour under reflux. After 24 more hours, a solution of $Mn(OAc)_2{\cdot}4H_2O$ (1.04 g, 4.27 mmol) in 10 mL of water was added to this reaction mixture, which remained under reflux for one more day. The solution was concentrated to one third of its initial volume and, after four weeks at room temperature, a mixture of deep-green crystals of $(Me_4N)_6[V_{15}O_{36}(Cl)]$ (Nunes *et al.*, 2012) and yellow prisms of **A** was obtained, the latter in 9% yield based on vanadium (56 mg). The FTIR spectrum recorded for **A** shows the characteristic bands of the Me_4N^+ cation at 3031, 1639, 1485 and 1263 cm^{-1} and of the inorganic anion at 966, 833, 744, 584 and 455 cm^{-1}.

Synthesis of $[NH_3C(CH_2OH)_3]_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]{\cdot}2H_2O$ (B)

A solution containing tris(hydroxymethyl)methylamine (0.720 g, 6.0 mmol) in 20 mL of water was added to a solution of NH_4VO_3 (1.17 g, 10.0 mmol) in the same volume of solvent. This reaction mixture was then refluxed until it became a clear solution, after which its pH was adjusted to 3 with aqueous HCl. A solution of $MnCl_2{\cdot}4H_2O$ (0.394 g, 2.0 mmol) in 10 mL of water was then added as a layer on top of the reaction mixture and, after two weeks at room temperature, yellow crystals of **B** were obtained (180 mg) in 12% yield based on vanadium. The FTIR spectrum of **B** shows characteristic bands of the $trisH^+$ cation at 3188, 2927, 2856, 1743, 1637, 1417, 1161 and 1112 cm^{-1} and of the inorganic anion at 941, 842 and 684 cm^{-1}.

Table 2
Hydrogen-bond geometry (Å, °) for compound **B**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O14^{i}	0.70 (12)	2.01 (12)	2.703 (7)	167 (12)
O1*W*—H1*B*···O12^{ii}	0.70 (7)	2.04 (8)	2.727 (8)	169 (8)
O2*W*—H2*A*···O5^{iii}	0.60 (7)	2.12 (7)	2.716 (7)	172 (9)
O2*W*—H2*B*···O12*A*	0.87 (10)	2.01 (10)	2.858 (8)	164 (8)
O3*W*—H3*A*···O7^{iii}	0.70 (9)	1.94 (9)	2.636 (7)	176 (10)
O3*W*—H3*B*···O11*A*^{iv}	0.88 (8)	1.91 (8)	2.752 (8)	160 (7)
O4*W*—H4*A*···O6^{v}	0.82 (11)	1.90 (11)	2.708 (6)	167 (10)
O4*W*—H4*B*···O2*W*^{v}	0.76 (9)	2.12 (9)	2.871 (7)	169 (9)
O5*W*—H5*A*···O8^{v}	0.55 (11)	2.18 (11)	2.725 (10)	170 (16)
O5*W*—H5*B*···O13*A*^{iv}	0.83 (14)	2.12 (13)	2.699 (12)	127 (12)
O5*W*—H5*B*···O13*B*^{iv}	0.83 (14)	1.95 (14)	2.77 (2)	168 (13)
N1—H1*C*···O3*W*^{v}	0.89	2.03	2.898 (7)	164
N1—H1*D*···O2	0.89	2.31	3.032 (7)	138
N1—H1*D*···O4*W*	0.89	2.45	3.105 (7)	130
N1—H1*E*···O4^{v}	0.89	1.91	2.787 (6)	166
C11—H11*C*···O11^{v}	0.97	2.46	3.392 (9)	160
O11*A*—H11*A*···O6*WA*^{v}	0.82	1.96	2.758 (12)	166
O12*A*—H12*A*···O3^{iii}	0.82	1.94	2.756 (7)	174
C13—H13*E*···O2	0.97	2.40	3.280 (10)	151
O13*B*—H13*B*···O6*WB*^{vi}	0.77	1.92	2.60 (2)	148
O6*WA*—H6*A*···O3	0.82 (2)	2.23 (9)	2.966 (9)	150 (15)
O6*WA*—H6*B*···O10^{vii}	0.82 (2)	2.16 (5)	2.952 (10)	165 (17)
O6*WB*—H6*C*···O3	0.82 (2)	2.03 (13)	2.802 (17)	156 (29)
O6*WB*—H6*D*···O10^{vii}	0.82 (2)	1.93 (8)	2.720 (19)	161 (24)

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

6. Refinement details

Crystal data, data collection and structure refinement details for the two structures are summarized in Table 3.

Hydrogen atoms on the cation were included in idealized positions (with methyl and methylene group C—H distances set at 0.96 and 0.97 Å, N—H at 0.89 Å and O—H at 0.82 Å) and their U_{iso} values were set to ride on the U_{eq} values of the parent atoms. Hydrogen atoms in the anions (on coordinating water molecules) were located in difference maps and were refined freely.

There are two independent solvent water molecules, one of which is disordered over two sites close to a centre of symmetry, in compound **A**. No hydrogen atoms were identified in these water molecules.

In **B**, there is one solvent water molecule which is disordered over two sites; the hydrogen atoms here were located in difference maps and were refined with distance restraints [O—H = 0.82 (2) Å].

Acknowledgements

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Table 3
Experimental details.

	Compound **A**	Compound **B**
Crystal data		
Chemical formula	$(C_4H_{12}N)_2\cdot[Mn_2V_{10}O_{28}(H_2O)_{10}]\cdot 5H_2O$	$(C_4H_{12}NO_3)_2[Mn_2V_{10}O_{28}(H_2O)_{10}]\cdot 2H_2O$
M_r	1485.81	1527.76
Crystal system, space group	Monoclinic, *I*2/*m*	Monoclinic, *C*2/*c*
Temperature (K)	292	295
a, *b*, *c* (Å)	13.2434 (7), 9.6402 (5), 17.7628 (13)	19.3147 (8), 9.7733 (4), 22.7952 (10)
β (°)	98.626 (2)	96.392 (1)
V (Å^3)	2242.1 (2)	4276.3 (3)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.64	2.78
Crystal size (mm)	0.48 × 0.38 × 0.15	0.49 × 0.26 × 0.13
Data collection		
Diffractometer	Bruker D8 Venture/Photon 100 CMOS	Bruker D8 Venture/Photon 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.562, 0.746	0.542, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	81983, 2953, 2752	71752, 3936, 3280
R_{int}	0.025	0.039
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.668	0.605
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.020, 0.060, 1.09	0.052, 0.114, 1.12
No. of reflections	2953	3936
No. of parameters	194	385
No. of restraints	0	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 2.2668P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0062P)^2 + 110.7865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.58, −0.34	0.78, −1.11

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXS97*, *SHELXL97* (Sheldrick, 2008), *SHELXL2013* and *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

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Crystal structures of two decavanadates(V) with pentaaquamanganese(II) pendant groups: $(NMe_4)_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 5H_2O$ and $[NH_3C(CH_2OH)_3]_2[V_{10}O_{28}\{Mn(H_2O)_5\}_2]\cdot 2H_2O$

Maurício P. Franco, André Luis Rüdiger, Jaísa F. Soares, Giovana G. Nunes and David L. Hughes

Computing details

For both compounds, data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for Compound-A; *SHELXS97* (Sheldrick 2008) for Compound-B. Program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015) for Compound-A; *SHELXL2014* (Sheldrick, 2015) for Compound-B. For both compounds, molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 2012).

(Compound-A) Bis(tetramethylammonium) decaaquadi-$\mu_4$oxido-tetra-μ_3-oxido-hexadeca-μ_2-oxido-hexaoxidodimanganesedecavanadate pentahydrate

Crystal data

$(C_4H_{12}N)_2\cdot[Mn_2V_{10}O_{28}(H_2O)_{10}]\cdot 5H_2O$
M_r = 1485.81
Monoclinic, $I2/m$
a = 13.2434 (7) Å
b = 9.6402 (5) Å
c = 17.7628 (13) Å
β = 98.626 (2)°
V = 2242.1 (2) Å^3
Z = 2
$F(000)$ = 1480
D_x = 2.201 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9256 reflections
θ = 3.1–28.3°
μ = 2.64 mm^{-1}
T = 292 K
Prism, yellow
0.48 × 0.38 × 0.15 mm

Data collection

Bruker D8 Venture/Photon 100 CMOS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.4167 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.562, T_{max} = 0.746
81983 measured reflections
2953 independent reflections
2752 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 28.4°, θ_{min} = 3.1°
$h = -17\rightarrow 17$
$k = -12\rightarrow 12$
$l = -23\rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.060$
$S = 1.09$
2953 reflections
194 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 2.2668P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.23106 (3)	0.5000	0.18528 (2)	0.02403 (8)	
V2	0.32741 (2)	0.5000	0.39643 (2)	0.01725 (8)	
V3	0.5000	0.66921 (3)	0.5000	0.01425 (8)	
V4	0.54714 (3)	0.5000	0.35620 (2)	0.01948 (8)	
V5	0.28084 (2)	0.65841 (2)	0.54017 (2)	0.02209 (7)	
O1	0.15020 (19)	0.5000	0.07177 (11)	0.0480 (6)	
O2	0.13101 (10)	0.32849 (12)	0.20645 (7)	0.0293 (2)	
O3	0.33574 (10)	0.33360 (12)	0.15931 (7)	0.0310 (3)	
O4	0.28574 (12)	0.5000	0.30500 (8)	0.0253 (3)	
O5	0.50366 (14)	0.5000	0.26708 (8)	0.0328 (4)	
O6	0.25845 (7)	0.36038 (10)	0.43170 (6)	0.0223 (2)	
O7	0.44883 (7)	0.62838 (10)	0.39540 (5)	0.01665 (18)	
O8	0.64321 (8)	0.36184 (11)	0.36540 (5)	0.0230 (2)	
O9	0.40458 (10)	0.5000	0.51485 (7)	0.0153 (2)	
O10	0.20825 (11)	0.5000	0.54989 (9)	0.0257 (3)	
O11	0.40317 (7)	0.77369 (10)	0.51675 (5)	0.02001 (19)	
O12	0.20299 (9)	0.78080 (13)	0.55243 (7)	0.0365 (3)	
H1A	0.1272 (17)	0.437 (2)	0.0491 (13)	0.053 (7)*	
H2A	0.1052 (16)	0.285 (2)	0.1767 (12)	0.038 (6)*	
H2B	0.1397 (15)	0.285 (2)	0.2440 (13)	0.038 (6)*	
H3A	0.3060 (19)	0.283 (3)	0.1339 (14)	0.053 (7)*	
H3B	0.392 (2)	0.359 (3)	0.1441 (17)	0.087 (10)*	
N1	0.85954 (17)	0.5000	0.23196 (11)	0.0348 (4)	
C10	0.9084 (2)	0.5000	0.16133 (14)	0.0373 (5)	
H10A	0.8883	0.4181	0.1321	0.056*	0.5
H10B	0.8870	0.5807	0.1315	0.056*	0.5
H10C	0.9813	0.5011	0.1750	0.056*	
C11	0.8902 (2)	0.3739 (2)	0.27733 (14)	0.0706 (8)	

H11A	0.8699	0.2930	0.2473	0.106*	
H11B	0.9630	0.3735	0.2920	0.106*	
H11C	0.8577	0.3735	0.3221	0.106*	
C12	0.7469 (3)	0.5000	0.2091 (2)	0.0895 (16)	
H12A	0.7269	0.4184	0.1797	0.134*	0.5
H12B	0.7142	0.5007	0.2539	0.134*	
H12C	0.7270	0.5810	0.1791	0.134*	0.5
O13	0.5022 (2)	0.3567 (5)	0.0856 (2)	0.1752 (17)	
O14A	0.5000	0.0973 (14)	0.0000	0.143 (14)	0.280 (18)
O14B	0.4760 (18)	0.0000	0.0562 (15)	0.158 (18)	0.220 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.03393 (17)	0.01631 (15)	0.01903 (15)	0.000	−0.00521 (12)	0.000
V2	0.01907 (15)	0.01704 (15)	0.01409 (15)	0.000	−0.00259 (11)	0.000
V3	0.01883 (15)	0.01043 (13)	0.01303 (14)	0.000	0.00088 (10)	0.000
V4	0.02432 (16)	0.02264 (17)	0.01183 (14)	0.000	0.00388 (11)	0.000
V5	0.02267 (12)	0.01995 (13)	0.02474 (13)	0.00444 (9)	0.00709 (9)	−0.00058 (9)
O1	0.0908 (17)	0.0167 (8)	0.0266 (9)	0.000	−0.0232 (9)	0.000
O2	0.0407 (6)	0.0190 (5)	0.0250 (6)	−0.0052 (4)	−0.0054 (5)	−0.0005 (4)
O3	0.0325 (6)	0.0240 (5)	0.0345 (6)	−0.0022 (5)	−0.0016 (5)	−0.0062 (5)
O4	0.0290 (7)	0.0270 (8)	0.0168 (6)	0.000	−0.0066 (5)	0.000
O5	0.0423 (9)	0.0413 (9)	0.0144 (7)	0.000	0.0030 (6)	0.000
O6	0.0219 (5)	0.0214 (5)	0.0223 (5)	−0.0047 (4)	−0.0010 (4)	−0.0013 (4)
O7	0.0214 (4)	0.0149 (4)	0.0128 (4)	0.0009 (3)	−0.0001 (3)	0.0016 (3)
O8	0.0285 (5)	0.0222 (5)	0.0195 (4)	0.0022 (4)	0.0078 (4)	−0.0029 (4)
O9	0.0191 (6)	0.0138 (6)	0.0128 (6)	0.000	0.0011 (5)	0.000
O10	0.0216 (7)	0.0268 (7)	0.0301 (8)	0.000	0.0082 (6)	0.000
O11	0.0256 (5)	0.0141 (4)	0.0202 (4)	0.0030 (4)	0.0031 (4)	−0.0001 (3)
O12	0.0341 (6)	0.0312 (6)	0.0458 (7)	0.0121 (5)	0.0113 (5)	−0.0029 (5)
N1	0.0484 (12)	0.0300 (10)	0.0304 (10)	0.000	0.0201 (9)	0.000
C10	0.0470 (14)	0.0381 (13)	0.0311 (12)	0.000	0.0204 (10)	0.000
C11	0.128 (2)	0.0406 (12)	0.0531 (13)	0.0137 (13)	0.0449 (15)	0.0168 (10)
C12	0.051 (2)	0.153 (5)	0.071 (3)	0.000	0.0329 (19)	0.000
O13	0.0805 (18)	0.238 (4)	0.220 (4)	0.022 (2)	0.064 (2)	0.065 (3)
O14A	0.027 (5)	0.059 (8)	0.33 (4)	0.000	−0.022 (10)	0.000
O14B	0.101 (15)	0.21 (4)	0.135 (19)	0.000	−0.077 (14)	0.000

Geometric parameters (Å, º)

Mn1—O1	2.1365 (18)	V5—O10	1.8264 (8)
Mn1—O4	2.1412 (14)	V5—O8^{iii}	1.8322 (10)
Mn1—O2	2.1863 (12)	V5—O6^{i}	1.9136 (10)
Mn1—O2^{i}	2.1863 (12)	V5—O11	2.0579 (10)
Mn1—O3	2.2136 (12)	V5—O9	2.3326 (10)
Mn1—O3^{i}	2.2136 (12)	V5—V5^{i}	3.0543 (5)
V2—O4	1.6350 (14)	V5—V4^{iii}	3.1068 (4)

V2—O6	1.7916 (10)	O1—H1A	0.76 (2)
V2—O6^{i}	1.7916 (10)	O2—H2A	0.72 (2)
V2—O7^{i}	2.0314 (10)	O2—H2B	0.78 (2)
V2—O7	2.0314 (10)	O3—H3A	0.74 (3)
V2—O9	2.1964 (12)	O3—H3B	0.87 (3)
V2—V4	3.0988 (5)	O6—V5^{i}	1.9137 (10)
V2—V5	3.1152 (4)	O8—V5^{iii}	1.8322 (10)
V2—V5^{i}	3.1153 (4)	O9—V3^{iii}	2.1041 (9)
V3—O11	1.6917 (10)	O9—V4^{iii}	2.2840 (12)
V3—O11^{ii}	1.6918 (10)	O9—V5^{i}	2.3327 (10)
V3—O7	1.9205 (9)	O10—V5^{i}	1.8264 (8)
V3—O7^{ii}	1.9205 (9)	N1—C11^{i}	1.481 (2)
V3—O9	2.1041 (9)	N1—C11	1.481 (2)
V3—O9^{iii}	2.1041 (9)	N1—C12	1.486 (4)
V3—V5	3.0928 (3)	N1—C10	1.496 (3)
V3—V5^{ii}	3.0928 (3)	C10—H10A	0.9600
V4—O5	1.6013 (15)	C10—H10B	0.9600
V4—O8^{i}	1.8322 (10)	C10—H10C	0.9600
V4—O8	1.8322 (10)	C11—H11A	0.9600
V4—O7	1.9959 (10)	C11—H11B	0.9600
V4—O7^{i}	1.9959 (10)	C11—H11C	0.9600
V4—O9^{iii}	2.2840 (12)	C12—H12A	0.9600
V4—V5^{ii}	3.1069 (4)	C12—H12B	0.9600
V4—V5^{iii}	3.1069 (4)	C12—H12C	0.9600
V5—O12	1.6030 (11)		

O1—Mn1—O4	169.83 (9)	O5—V4—V5^{iii}	135.13 (5)
O1—Mn1—O2	86.07 (6)	O8^{i}—V4—V5^{iii}	82.35 (3)
O4—Mn1—O2	87.28 (4)	O8—V4—V5^{iii}	32.02 (3)
O1—Mn1—O2^{i}	86.07 (6)	O7—V4—V5^{iii}	123.83 (3)
O4—Mn1—O2^{i}	87.28 (4)	O7^{i}—V4—V5^{iii}	86.97 (3)
O2—Mn1—O2^{i}	98.27 (7)	O9^{iii}—V4—V5^{iii}	48.37 (3)
O1—Mn1—O3	92.53 (6)	V2—V4—V5^{iii}	119.596 (11)
O4—Mn1—O3	94.47 (4)	V5^{ii}—V4—V5^{iii}	58.884 (11)
O2—Mn1—O3	84.40 (5)	O12—V5—O10	104.13 (6)
O2^{i}—Mn1—O3	176.89 (5)	O12—V5—O8^{iii}	103.30 (6)
O1—Mn1—O3^{i}	92.53 (6)	O10—V5—O8^{iii}	92.80 (6)
O4—Mn1—O3^{i}	94.47 (4)	O12—V5—O6^{i}	101.58 (6)
O2—Mn1—O3^{i}	176.88 (5)	O10—V5—O6^{i}	90.67 (6)
O2^{i}—Mn1—O3^{i}	84.40 (5)	O8^{iii}—V5—O6^{i}	153.19 (5)
O3—Mn1—O3^{i}	92.89 (7)	O12—V5—O11	99.90 (6)
O4—V2—O6	103.51 (5)	O10—V5—O11	155.80 (5)
O4—V2—O6^{i}	103.51 (5)	O8^{iii}—V5—O11	84.37 (4)
O6—V2—O6^{i}	97.40 (7)	O6^{i}—V5—O11	81.68 (4)
O4—V2—O7^{i}	98.09 (5)	O12—V5—O9	173.12 (5)
O6—V2—O7^{i}	89.49 (4)	O10—V5—O9	82.29 (4)
O6^{i}—V2—O7^{i}	155.03 (4)	O8^{iii}—V5—O9	78.56 (4)
O4—V2—O7	98.09 (5)	O6^{i}—V5—O9	75.59 (4)

O6—V2—O7	155.03 (4)	O11—V5—O9	73.59 (3)
O6^{i}—V2—O7	89.49 (4)	O12—V5—V5^{i}	137.39 (5)
O7^{i}—V2—O7	75.07 (5)	O10—V5—V5^{i}	33.27 (4)
O4—V2—O9	172.10 (7)	O8^{iii}—V5—V5^{i}	83.88 (3)
O6—V2—O9	81.57 (4)	O6^{i}—V5—V5^{i}	84.57 (3)
O6^{i}—V2—O9	81.57 (4)	O11—V5—V5^{i}	122.69 (3)
O7^{i}—V2—O9	75.72 (4)	O9—V5—V5^{i}	49.10 (2)
O7—V2—O9	75.72 (4)	O12—V5—V3	130.66 (5)
O4—V2—V4	87.69 (6)	O10—V5—V3	125.13 (4)
O6—V2—V4	128.77 (3)	O8^{iii}—V5—V3	79.01 (3)
O6^{i}—V2—V4	128.77 (3)	O6^{i}—V5—V3	77.29 (3)
O7^{i}—V2—V4	39.28 (3)	O11—V5—V3	30.76 (3)
O7—V2—V4	39.28 (3)	O9—V5—V3	42.84 (2)
O9—V2—V4	84.41 (4)	V5^{i}—V5—V3	91.929 (7)
O4—V2—V5	137.34 (4)	O12—V5—V4^{iii}	135.29 (5)
O6—V2—V5	84.70 (3)	O10—V5—V4^{iii}	83.26 (4)
O6^{i}—V2—V5	34.01 (3)	O8^{iii}—V5—V4^{iii}	32.02 (3)
O7^{i}—V2—V5	124.08 (3)	O6^{i}—V5—V4^{iii}	122.63 (3)
O7—V2—V5	87.88 (3)	O11—V5—V4^{iii}	81.71 (3)
O9—V2—V5	48.39 (3)	O9—V5—V4^{iii}	47.04 (3)
V4—V2—V5	119.816 (10)	V5^{i}—V5—V4^{iii}	60.558 (6)
O4—V2—V5^{i}	137.34 (4)	V3—V5—V4^{iii}	61.520 (9)
O6—V2—V5^{i}	34.02 (3)	O12—V5—V2	133.04 (5)
O6^{i}—V2—V5^{i}	84.70 (3)	O10—V5—V2	80.75 (4)
O7^{i}—V2—V5^{i}	87.88 (3)	O8^{iii}—V5—V2	123.30 (3)
O7—V2—V5^{i}	124.08 (3)	O6^{i}—V5—V2	31.58 (3)
O9—V2—V5^{i}	48.39 (3)	O11—V5—V2	80.81 (3)
V4—V2—V5^{i}	119.816 (10)	O9—V5—V2	44.75 (3)
V5—V2—V5^{i}	58.710 (11)	V5^{i}—V5—V2	60.645 (6)
O11—V3—O11^{ii}	106.92 (7)	V3—V5—V2	61.274 (8)
O11—V3—O7	97.20 (4)	V4^{iii}—V5—V2	91.545 (10)
O11^{ii}—V3—O7	96.82 (4)	Mn1—O1—H1A	127.0 (17)
O11—V3—O7^{ii}	96.82 (4)	Mn1—O2—H2A	123.2 (17)
O11^{ii}—V3—O7^{ii}	97.20 (4)	Mn1—O2—H2B	122.5 (15)
O7—V3—O7^{ii}	156.35 (6)	H2A—O2—H2B	108 (2)
O11—V3—O9	87.37 (4)	Mn1—O3—H3A	108.1 (19)
O11^{ii}—V3—O9	165.69 (5)	Mn1—O3—H3B	117 (2)
O7—V3—O9	80.27 (4)	H3A—O3—H3B	114 (3)
O7^{ii}—V3—O9	81.45 (4)	V2—O4—Mn1	179.96 (10)
O11—V3—O9^{iii}	165.69 (5)	V2—O6—V5^{i}	114.40 (5)
O11^{ii}—V3—O9^{iii}	87.38 (4)	V3—O7—V4	108.10 (4)
O7—V3—O9^{iii}	81.45 (4)	V3—O7—V2	106.33 (4)
O7^{ii}—V3—O9^{iii}	80.27 (4)	V4—O7—V2	100.60 (4)
O9—V3—O9^{iii}	78.34 (6)	V5^{iii}—O8—V4	115.96 (5)
O11—V3—V5	38.47 (3)	V3^{iii}—O9—V3	101.66 (6)
O11^{ii}—V3—V5	145.38 (4)	V3^{iii}—O9—V2	94.70 (4)
O7—V3—V5	90.52 (3)	V3—O9—V2	94.70 (4)
O7^{ii}—V3—V5	88.69 (3)	V3^{iii}—O9—V4^{iii}	92.45 (4)

O9—V3—V5	48.93 (3)	V3—O9—V4^{iii}	92.45 (4)
O9^{iii}—V3—V5	127.22 (3)	V2—O9—V4^{iii}	168.68 (7)
O11—V3—V5^{ii}	145.38 (4)	V3^{iii}—O9—V5	169.81 (5)
O11^{ii}—V3—V5^{ii}	38.47 (3)	V3—O9—V5	88.231 (11)
O7—V3—V5^{ii}	88.68 (3)	V2—O9—V5	86.86 (4)
O7^{ii}—V3—V5^{ii}	90.52 (3)	V4^{iii}—O9—V5	84.59 (4)
O9—V3—V5^{ii}	127.22 (3)	V3^{iii}—O9—V5^{i}	88.232 (11)
O9^{iii}—V3—V5^{ii}	48.93 (3)	V3—O9—V5^{i}	169.81 (5)
V5—V3—V5^{ii}	176.145 (13)	V2—O9—V5^{i}	86.86 (4)
O5—V4—O8^{i}	103.31 (5)	V4^{iii}—O9—V5^{i}	84.59 (4)
O5—V4—O8	103.30 (5)	V5—O9—V5^{i}	81.79 (4)
O8^{i}—V4—O8	93.26 (7)	V5^{i}—O10—V5	113.47 (8)
O5—V4—O7	100.85 (6)	V3—O11—V5	110.76 (5)
O8^{i}—V4—O7	89.92 (4)	C11^{i}—N1—C11	110.3 (3)
O8—V4—O7	154.18 (4)	C11^{i}—N1—C12	109.32 (18)
O5—V4—O7^{i}	100.85 (6)	C11—N1—C12	109.32 (18)
O8^{i}—V4—O7^{i}	154.18 (4)	C11^{i}—N1—C10	109.79 (14)
O8—V4—O7^{i}	89.92 (4)	C11—N1—C10	109.79 (14)
O7—V4—O7^{i}	76.64 (6)	C12—N1—C10	108.3 (2)
O5—V4—O9^{iii}	175.24 (8)	N1—C10—H10A	109.5
O8^{i}—V4—O9^{iii}	79.88 (4)	N1—C10—H10B	109.5
O8—V4—O9^{iii}	79.88 (4)	H10A—C10—H10B	109.5
O7—V4—O9^{iii}	75.47 (4)	N1—C10—H10C	109.5
O7^{i}—V4—O9^{iii}	75.48 (4)	H10A—C10—H10C	109.5
O5—V4—V2	90.98 (7)	H10B—C10—H10C	109.5
O8^{i}—V4—V2	130.01 (3)	N1—C11—H11A	109.5
O8—V4—V2	130.01 (3)	N1—C11—H11B	109.5
O7—V4—V2	40.12 (3)	H11A—C11—H11B	109.5
O7^{i}—V4—V2	40.12 (3)	N1—C11—H11C	109.5
O9^{iii}—V4—V2	84.26 (3)	H11A—C11—H11C	109.5
O5—V4—V5^{ii}	135.13 (5)	H11B—C11—H11C	109.5
O8^{i}—V4—V5^{ii}	32.02 (3)	N1—C12—H12A	109.5
O8—V4—V5^{ii}	82.35 (3)	N1—C12—H12B	109.5
O7—V4—V5^{ii}	86.97 (3)	H12A—C12—H12B	109.5
O7^{i}—V4—V5^{ii}	123.83 (3)	N1—C12—H12C	109.5
O9^{iii}—V4—V5^{ii}	48.37 (3)	H12A—C12—H12C	109.5
V2—V4—V5^{ii}	119.596 (11)	H12B—C12—H12C	109.5

O4—V2—O6—V5^{i}	−174.84 (6)	O12—V5—O10—V5^{i}	−178.86 (8)
O6^{i}—V2—O6—V5^{i}	−68.97 (7)	O8^{iii}—V5—O10—V5^{i}	−74.39 (8)
O7^{i}—V2—O6—V5^{i}	86.96 (6)	O6^{i}—V5—O10—V5^{i}	79.02 (8)
O7—V2—O6—V5^{i}	35.96 (13)	O11—V5—O10—V5^{i}	8.1 (2)
O9—V2—O6—V5^{i}	11.32 (5)	O9—V5—O10—V5^{i}	3.67 (8)
V4—V2—O6—V5^{i}	87.13 (6)	V3—V5—O10—V5^{i}	4.14 (11)
V5—V2—O6—V5^{i}	−37.34 (5)	V4^{iii}—V5—O10—V5^{i}	−43.77 (7)
O5—V4—O8—V5^{iii}	174.45 (7)	V2—V5—O10—V5^{i}	48.91 (7)
O8^{i}—V4—O8—V5^{iii}	69.96 (7)	O11^{ii}—V3—O11—V5	−178.88 (6)
O7—V4—O8—V5^{iii}	−26.63 (13)	O7—V3—O11—V5	81.71 (5)

O7^{i}—V4—O8—V5^{iii}	−84.41 (6)	O7^{ii}—V3—O11—V5	−79.19 (5)
O9^{iii}—V4—O8—V5^{iii}	−9.15 (5)	O9—V3—O11—V5	1.87 (5)
V2—V4—O8—V5^{iii}	−82.75 (6)	O9^{iii}—V3—O11—V5	−1.9 (2)
V5^{ii}—V4—O8—V5^{iii}	39.78 (5)	V5^{ii}—V3—O11—V5	179.893 (6)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O11^{iv}	0.76 (2)	1.97 (2)	2.7199 (14)	168 (2)
O2—H2*A*···O7^{iv}	0.72 (2)	2.04 (2)	2.7457 (15)	167 (2)
O2—H2*B*···O3^{v}	0.78 (2)	2.05 (2)	2.8295 (18)	178 (2)
O3—H3*A*···O6^{v}	0.74 (3)	1.92 (3)	2.6573 (16)	174 (3)
O3—H3*B*···O13	0.87 (3)	1.91 (3)	2.737 (3)	158 (3)
C10—H10*A*···O11^{vi}	0.96	2.51	3.362 (2)	148
C10—H10*B*···O11^{vii}	0.96	2.51	3.362 (2)	148
C10—H10*C*···O2^{viii}	0.96	2.58	3.370 (3)	139
C10—H10*C*···O2^{ix}	0.96	2.57	3.370 (3)	141
C11—H11*A*···O8^{x}	0.96	2.48	3.384 (3)	156
C12—H12*A*···O12^{vi}	0.96	2.60	3.474 (4)	152
C12—H12*C*···O12^{vii}	0.96	2.59	3.474 (4)	153

Symmetry codes: (iv) $-x+1/2$, $y-1/2$, $-z+1/2$; (v) $-x+1/2$, $-y+1/2$, $-z+1/2$; (vi) $x+1/2$, $y-1/2$, $z-1/2$; (vii) $x+1/2$, $-y+3/2$, $z-1/2$; (viii) $x+1$, y, z; (ix) $x+1$, $-y+1$, z; (x) $-x+3/2$, $-y+1/2$, $-z+1/2$.

(Compound-B) Bis{[tris(hydroxymethyl)methyl]ammonium} decaaquadi-$\mu_4$oxido-tetra-μ_3-oxido-hexadeca-μ_2-oxido-hexaoxidodimanganesedecavanadate dihydrate

Crystal data

$(C_4H_{12}NO_3)_2[Mn_2V_{10}O_{28}(H_2O)_{10}]\cdot 2H_2O$
M_r = 1527.76
Monoclinic, $C2/c$
a = 19.3147 (8) Å
b = 9.7733 (4) Å
c = 22.7952 (10) Å
β = 96.392 (1)°
V = 4276.3 (3) Å^3
Z = 4
$F(000)$ = 3032
D_x = 2.373 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 38099 reflections
θ = 3.0–25.4°
μ = 2.78 mm^{-1}
T = 295 K
Plate, yellow
0.49 × 0.26 × 0.13 mm

Data collection

Bruker D8 Venture/Photon 100 CMOS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.4167 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)
T_{min} = 0.542, T_{max} = 0.745
71752 measured reflections
3936 independent reflections
3280 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 25.5°, θ_{min} = 2.9°
$h = -23\rightarrow 23$
$k = -11\rightarrow 11$
$l = -27\rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.114$
$S = 1.12$
3936 reflections
385 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0062P)^2 + 110.7865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -1.11$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.80093 (5)	0.43409 (10)	0.18078 (4)	0.0239 (2)	
V2	0.60396 (5)	0.43006 (10)	0.17920 (4)	0.0172 (2)	
V3	0.62652 (5)	0.43454 (11)	0.31542 (4)	0.0182 (2)	
V4	0.47896 (5)	0.58914 (11)	0.11421 (5)	0.0226 (3)	
V5	0.47615 (5)	0.27690 (11)	0.11376 (5)	0.0222 (2)	
V6	0.5000	0.59971 (13)	0.2500	0.0165 (3)	
V7	0.5000	0.26656 (14)	0.2500	0.0153 (3)	
O1	0.6885 (2)	0.4257 (4)	0.17944 (18)	0.0228 (9)	
O2	0.7094 (2)	0.4358 (5)	0.31283 (18)	0.0239 (9)	
O3	0.5769 (2)	0.5689 (4)	0.12912 (18)	0.0223 (9)	
O4	0.5757 (2)	0.2948 (4)	0.12929 (18)	0.0195 (9)	
O5	0.59743 (19)	0.5594 (4)	0.24810 (17)	0.0185 (8)	
O6	0.59724 (18)	0.3057 (4)	0.24851 (17)	0.0148 (8)	
O7	0.6131 (2)	0.5718 (4)	0.36695 (18)	0.0234 (9)	
O8	0.6144 (2)	0.2967 (4)	0.36707 (18)	0.0220 (9)	
O9	0.4718 (3)	0.7085 (5)	0.0667 (2)	0.0362 (12)	
O10	0.4714 (2)	0.4332 (5)	0.06979 (18)	0.0255 (9)	
O11	0.4680 (2)	0.1569 (5)	0.0664 (2)	0.0324 (11)	
O12	0.4913 (2)	0.7043 (4)	0.19037 (19)	0.0251 (10)	
O13	0.49147 (19)	0.4337 (4)	0.19135 (17)	0.0157 (8)	
O14	0.4907 (2)	0.1636 (4)	0.18997 (18)	0.0186 (9)	
O1W	0.9115 (3)	0.4350 (7)	0.1854 (4)	0.056 (2)	
O2W	0.8106 (3)	0.2701 (6)	0.2493 (2)	0.0282 (12)	
O3W	0.7972 (3)	0.2741 (5)	0.1120 (2)	0.0260 (10)	
O4W	0.8094 (3)	0.5982 (5)	0.2475 (2)	0.0255 (10)	
O5W	0.7904 (4)	0.5909 (8)	0.1149 (3)	0.0463 (17)	
H1A	0.929 (6)	0.497 (12)	0.182 (5)	0.08 (4)*	
H1B	0.936 (4)	0.383 (8)	0.187 (3)	0.015 (19)*	

H2A	0.832 (4)	0.227 (8)	0.248 (3)	0.01 (2)*	
H2B	0.820 (5)	0.297 (10)	0.286 (4)	0.06 (3)*	
H3A	0.820 (5)	0.220 (10)	0.119 (4)	0.05 (3)*	
H3B	0.799 (4)	0.295 (8)	0.075 (4)	0.03 (2)*	
H4A	0.841 (6)	0.653 (11)	0.245 (4)	0.08 (4)*	
H4B	0.775 (5)	0.636 (9)	0.245 (4)	0.04 (3)*	
H5A	0.812 (6)	0.626 (12)	0.119 (5)	0.06 (5)*	
H5B	0.774 (7)	0.564 (14)	0.082 (6)	0.11 (5)*	
N1	0.8230 (3)	0.5979 (5)	0.3845 (2)	0.0246 (12)	
H1C	0.7881	0.6509	0.3932	0.029*	
H1D	0.8090	0.5474	0.3529	0.029*	
H1E	0.8588	0.6500	0.3770	0.029*	
C10	0.8451 (3)	0.5061 (7)	0.4357 (3)	0.0275 (14)	
C11	0.8775 (4)	0.5944 (7)	0.4861 (3)	0.0341 (16)	
H11B	0.8885	0.5386	0.5211	0.041*	
H11C	0.9205	0.6343	0.4758	0.041*	
O11A	0.8302 (3)	0.7007 (6)	0.4981 (3)	0.0517 (15)	
H11A	0.8462	0.7751	0.4899	0.078*	
C12	0.8985 (4)	0.4081 (8)	0.4159 (4)	0.047 (2)	
H12B	0.9374	0.4588	0.4034	0.056*	
H12C	0.9159	0.3489	0.4484	0.056*	
O12A	0.8665 (4)	0.3279 (6)	0.3681 (3)	0.0591 (18)	
H12A	0.8860	0.2534	0.3679	0.089*	
C13	0.7796 (5)	0.4328 (9)	0.4506 (4)	0.050 (2)	
H13C	0.7442	0.4997	0.4573	0.061*	0.694 (13)
H13D	0.7615	0.3755	0.4177	0.061*	0.694 (13)
H13E	0.7442	0.4383	0.4170	0.061*	0.306 (13)
H13F	0.7902	0.3369	0.4580	0.061*	0.306 (13)
O13A	0.7939 (7)	0.3553 (10)	0.4991 (4)	0.073 (4)	0.694 (13)
H13A	0.8064	0.2791	0.4896	0.110*	0.694 (13)
O13B	0.7539 (9)	0.487 (3)	0.4988 (9)	0.062 (8)	0.306 (13)
H13B	0.73 (2)	0.44 (3)	0.510 (12)	0.093*	0.306 (13)
O6WA	0.6367 (5)	0.4696 (11)	0.0226 (4)	0.051 (3)	0.694 (13)
H6A	0.617 (6)	0.465 (16)	0.053 (3)	0.077*	0.694 (13)
H6B	0.612 (6)	0.509 (16)	−0.003 (4)	0.077*	0.694 (13)
O6WB	0.6316 (9)	0.596 (3)	0.0209 (8)	0.046 (6)	0.306 (13)
H6C	0.627 (13)	0.58 (4)	0.055 (4)	0.069*	0.306 (13)
H6D	0.595 (8)	0.58 (3)	0.000 (8)	0.069*	0.306 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0168 (4)	0.0170 (5)	0.0383 (6)	−0.0012 (4)	0.0049 (4)	−0.0002 (4)
V2	0.0119 (4)	0.0152 (5)	0.0248 (5)	0.0002 (4)	0.0037 (4)	0.0007 (4)
V3	0.0119 (4)	0.0167 (5)	0.0258 (5)	−0.0004 (4)	0.0012 (4)	−0.0009 (4)
V4	0.0206 (5)	0.0193 (6)	0.0279 (6)	0.0007 (4)	0.0024 (4)	0.0071 (4)
V5	0.0191 (5)	0.0225 (6)	0.0252 (6)	−0.0010 (4)	0.0029 (4)	−0.0040 (4)
V6	0.0137 (7)	0.0058 (6)	0.0301 (8)	0.000	0.0025 (6)	0.000

V7	0.0103 (6)	0.0120 (7)	0.0240 (7)	0.000	0.0029 (5)	0.000
O1	0.0148 (19)	0.022 (2)	0.032 (2)	0.0009 (18)	0.0057 (17)	0.0007 (19)
O2	0.0143 (19)	0.027 (2)	0.030 (2)	0.0033 (19)	0.0016 (17)	−0.0001 (19)
O3	0.020 (2)	0.021 (2)	0.027 (2)	−0.0017 (19)	0.0046 (17)	0.0027 (19)
O4	0.017 (2)	0.016 (2)	0.026 (2)	0.0000 (17)	0.0064 (17)	−0.0027 (18)
O5	0.0172 (19)	0.014 (2)	0.024 (2)	0.0007 (17)	0.0026 (16)	−0.0001 (17)
O6	0.0073 (17)	0.0087 (19)	0.029 (2)	0.0015 (15)	0.0031 (15)	0.0002 (16)
O7	0.020 (2)	0.021 (2)	0.028 (2)	−0.0034 (19)	0.0000 (17)	−0.0054 (19)
O8	0.016 (2)	0.020 (2)	0.029 (2)	0.0006 (17)	0.0030 (17)	0.0019 (18)
O9	0.035 (3)	0.032 (3)	0.041 (3)	0.000 (2)	0.002 (2)	0.019 (2)
O10	0.022 (2)	0.031 (2)	0.023 (2)	0.000 (2)	0.0011 (17)	0.005 (2)
O11	0.027 (2)	0.036 (3)	0.034 (3)	−0.004 (2)	0.002 (2)	−0.009 (2)
O12	0.022 (2)	0.019 (2)	0.034 (3)	0.0004 (19)	0.0054 (18)	0.0065 (19)
O13	0.0134 (18)	0.0105 (18)	0.023 (2)	0.0000 (17)	0.0030 (15)	0.0035 (16)
O14	0.0148 (19)	0.0076 (18)	0.034 (2)	−0.0003 (16)	0.0046 (17)	−0.0011 (17)
O1W	0.016 (3)	0.014 (3)	0.139 (7)	0.002 (3)	0.013 (3)	0.002 (3)
O2W	0.031 (3)	0.021 (3)	0.033 (3)	0.010 (2)	0.005 (2)	0.000 (2)
O3W	0.026 (3)	0.017 (2)	0.035 (3)	0.002 (2)	0.004 (2)	0.001 (2)
O4W	0.015 (2)	0.018 (2)	0.045 (3)	−0.003 (2)	0.007 (2)	−0.004 (2)
O5W	0.055 (4)	0.038 (4)	0.046 (4)	−0.014 (3)	0.003 (3)	0.007 (3)
N1	0.024 (3)	0.015 (3)	0.035 (3)	−0.004 (2)	0.002 (2)	−0.001 (2)
C10	0.032 (4)	0.020 (3)	0.030 (3)	0.001 (3)	0.001 (3)	0.002 (3)
C11	0.037 (4)	0.034 (4)	0.031 (4)	−0.002 (3)	0.003 (3)	−0.004 (3)
O11A	0.082 (4)	0.033 (3)	0.039 (3)	0.010 (3)	0.002 (3)	−0.013 (3)
C12	0.049 (5)	0.041 (5)	0.046 (5)	0.018 (4)	−0.012 (4)	−0.008 (4)
O12A	0.082 (5)	0.043 (3)	0.046 (3)	0.038 (3)	−0.020 (3)	−0.021 (3)
C13	0.069 (6)	0.040 (5)	0.045 (5)	−0.030 (5)	0.020 (4)	−0.005 (4)
O13A	0.122 (10)	0.053 (6)	0.041 (5)	−0.038 (7)	−0.005 (5)	0.013 (4)
O13B	0.010 (8)	0.13 (2)	0.049 (11)	−0.012 (10)	0.010 (7)	−0.020 (13)
O6WA	0.059 (6)	0.061 (7)	0.035 (5)	0.007 (5)	0.009 (4)	0.002 (4)
O6WB	0.024 (9)	0.081 (18)	0.034 (10)	−0.008 (10)	0.007 (7)	0.001 (10)

Geometric parameters (Å, º)

Mn1—O1W	2.126 (5)	V7—O6	1.921 (4)
Mn1—O5W	2.139 (7)	V7—O6^{i}	1.921 (4)
Mn1—O1	2.169 (4)	V7—O13	2.106 (4)
Mn1—O4W	2.204 (5)	V7—O13^{i}	2.106 (4)
Mn1—O3W	2.209 (5)	V7—V5^{i}	3.0900 (11)
Mn1—O2W	2.231 (5)	O7—V4^{i}	1.884 (4)
V2—O1	1.634 (4)	O8—V5^{i}	1.860 (4)
V2—O4	1.789 (4)	O13—V3^{i}	2.267 (4)
V2—O3	1.812 (4)	O1W—H1A	0.70 (12)
V2—O6	2.009 (4)	O1W—H1B	0.70 (7)
V2—O5	2.031 (4)	O2W—H2A	0.60 (7)
V2—O13	2.221 (4)	O2W—H2B	0.87 (10)
V2—V3	3.0875 (14)	O3W—H3A	0.70 (9)
V2—V4	3.1056 (14)	O3W—H3B	0.88 (8)

V3—O2	1.609 (4)	O4W—H4A	0.82 (11)
V3—O7	1.821 (4)	O4W—H4B	0.76 (9)
V3—O8	1.821 (4)	O5W—H5A	0.55 (11)
V3—O5	1.992 (4)	O5W—H5B	0.83 (14)
V3—O6	2.010 (4)	N1—C10	1.496 (8)
V3—O13^{i}	2.267 (4)	N1—H1C	0.8900
V3—V5^{i}	3.1025 (14)	N1—H1D	0.8900
V4—O9	1.587 (5)	N1—H1E	0.8900
V4—O10	1.826 (5)	C10—C12	1.513 (10)
V4—O7^{i}	1.884 (4)	C10—C11	1.517 (9)
V4—O3	1.895 (4)	C10—C13	1.525 (10)
V4—O12	2.061 (5)	C11—O11A	1.431 (9)
V4—O13	2.316 (4)	C11—H11B	0.9700
V4—V5	3.0521 (15)	C11—H11C	0.9700
V4—V6	3.0786 (11)	O11A—H11A	0.8200
V5—O11	1.590 (5)	C12—O12A	1.426 (9)
V5—O10	1.824 (5)	C12—H12B	0.9700
V5—O8^{i}	1.860 (4)	C12—H12C	0.9700
V5—O4	1.925 (4)	O12A—H12A	0.8200
V5—O14	2.053 (4)	C13—O13A	1.343 (12)
V5—O13	2.334 (4)	C13—O13B	1.36 (2)
V5—V7	3.0900 (11)	C13—H13C	0.9700
V5—V3^{i}	3.1025 (14)	C13—H13D	0.9700
V6—O12	1.694 (4)	C13—H13E	0.9700
V6—O12^{i}	1.694 (4)	C13—H13F	0.9700
V6—O5	1.928 (4)	O13A—H13A	0.8200
V6—O5^{i}	1.928 (4)	O13B—H13B	0.8 (4)
V6—O13^{i}	2.097 (4)	O6WA—H6A	0.82 (2)
V6—O13	2.097 (4)	O6WA—H6B	0.82 (2)
V6—V4^{i}	3.0786 (11)	O6WB—H6C	0.82 (2)
V7—O14	1.692 (4)	O6WB—H6D	0.82 (2)
V7—O14^{i}	1.692 (4)		

O1W—Mn1—O5W	92.8 (3)	O12—V6—O12^{i}	105.8 (3)
O1W—Mn1—O1	177.2 (2)	O12—V6—O5	96.61 (19)
O5W—Mn1—O1	90.0 (3)	O12^{i}—V6—O5	97.57 (19)
O1W—Mn1—O4W	88.0 (2)	O12—V6—O5^{i}	97.57 (19)
O5W—Mn1—O4W	87.5 (3)	O12^{i}—V6—O5^{i}	96.61 (19)
O1—Mn1—O4W	91.99 (18)	O5—V6—O5^{i}	156.4 (3)
O1W—Mn1—O3W	89.5 (2)	O12—V6—O13^{i}	166.4 (2)
O5W—Mn1—O3W	90.9 (3)	O12^{i}—V6—O13^{i}	87.80 (18)
O1—Mn1—O3W	90.57 (17)	O5—V6—O13^{i}	81.29 (16)
O4W—Mn1—O3W	177.02 (19)	O5^{i}—V6—O13^{i}	80.50 (16)
O1W—Mn1—O2W	87.9 (3)	O12—V6—O13	87.80 (18)
O5W—Mn1—O2W	179.3 (3)	O12^{i}—V6—O13	166.4 (2)
O1—Mn1—O2W	89.35 (19)	O5—V6—O13	80.50 (16)
O4W—Mn1—O2W	92.61 (19)	O5^{i}—V6—O13	81.28 (16)
O3W—Mn1—O2W	88.9 (2)	O13^{i}—V6—O13	78.6 (2)

O1—V2—O4	102.5 (2)	O12—V6—V4	39.04 (15)
O1—V2—O3	103.9 (2)	O12^{i}—V6—V4	144.81 (16)
O4—V2—O3	96.10 (18)	O5—V6—V4	89.45 (12)
O1—V2—O6	97.69 (18)	O5^{i}—V6—V4	89.76 (12)
O4—V2—O6	90.65 (17)	O13^{i}—V6—V4	127.39 (11)
O3—V2—O6	155.37 (17)	O13—V6—V4	48.76 (10)
O1—V2—O5	99.30 (19)	O12—V6—V4^{i}	144.81 (16)
O4—V2—O5	155.64 (17)	O12^{i}—V6—V4^{i}	39.04 (15)
O3—V2—O5	89.03 (18)	O5—V6—V4^{i}	89.76 (12)
O6—V2—O5	75.72 (15)	O5^{i}—V6—V4^{i}	89.45 (12)
O1—V2—O13	172.67 (19)	O13^{i}—V6—V4^{i}	48.76 (10)
O4—V2—O13	81.85 (16)	O13—V6—V4^{i}	127.39 (11)
O3—V2—O13	81.31 (16)	V4—V6—V4^{i}	176.15 (6)
O6—V2—O13	76.23 (14)	O14—V7—O14^{i}	107.0 (3)
O5—V2—O13	75.39 (15)	O14—V7—O6	96.90 (17)
O1—V2—V3	88.16 (15)	O14^{i}—V7—O6	96.68 (17)
O4—V2—V3	130.47 (14)	O14—V7—O6^{i}	96.68 (17)
O3—V2—V3	128.43 (14)	O14^{i}—V7—O6^{i}	96.90 (17)
O6—V2—V3	39.82 (11)	O6—V7—O6^{i}	157.1 (2)
O5—V2—V3	39.40 (12)	O14—V7—O13	87.36 (17)
O13—V2—V3	84.54 (10)	O14^{i}—V7—O13	165.61 (18)
O1—V2—V4	137.61 (16)	O6—V7—O13	80.91 (15)
O4—V2—V4	84.31 (13)	O6^{i}—V7—O13	81.34 (15)
O3—V2—V4	33.93 (13)	O14—V7—O13^{i}	165.61 (18)
O6—V2—V4	124.28 (11)	O14^{i}—V7—O13^{i}	87.36 (17)
O5—V2—V4	86.88 (11)	O6—V7—O13^{i}	81.34 (15)
O13—V2—V4	48.09 (10)	O6^{i}—V7—O13^{i}	80.91 (15)
V3—V2—V4	119.20 (4)	O13—V7—O13^{i}	78.3 (2)
O2—V3—O7	103.4 (2)	O14—V7—V5	38.37 (13)
O2—V3—O8	103.3 (2)	O14^{i}—V7—V5	145.37 (15)
O7—V3—O8	95.17 (19)	O6—V7—V5	90.71 (12)
O2—V3—O5	99.42 (19)	O6^{i}—V7—V5	88.54 (12)
O7—V3—O5	89.87 (18)	O13—V7—V5	49.01 (11)
O8—V3—O5	154.91 (18)	O13^{i}—V7—V5	127.24 (12)
O2—V3—O6	100.03 (19)	O14—V7—V5^{i}	145.37 (15)
O7—V3—O6	154.59 (17)	O14^{i}—V7—V5^{i}	38.37 (13)
O8—V3—O6	88.95 (18)	O6—V7—V5^{i}	88.54 (12)
O5—V3—O6	76.57 (15)	O6^{i}—V7—V5^{i}	90.71 (12)
O2—V3—O13^{i}	174.03 (19)	O13—V7—V5^{i}	127.24 (12)
O7—V3—O13^{i}	80.37 (16)	O13^{i}—V7—V5^{i}	49.01 (11)
O8—V3—O13^{i}	80.84 (16)	V5—V7—V5^{i}	176.25 (7)
O5—V3—O13^{i}	75.79 (15)	V2—O1—Mn1	176.3 (3)
O6—V3—O13^{i}	75.54 (14)	V2—O3—V4	113.8 (2)
O2—V3—V2	89.59 (15)	V2—O4—V5	114.3 (2)
O7—V3—V2	130.18 (15)	V6—O5—V3	107.48 (19)
O8—V3—V2	128.75 (14)	V6—O5—V2	106.83 (18)
O5—V3—V2	40.33 (12)	V3—O5—V2	100.27 (18)
O6—V3—V2	39.80 (11)	V7—O6—V2	106.44 (18)

O13^{i}—V3—V2	84.45 (10)	V7—O6—V3	107.72 (18)
O2—V3—V5^{i}	136.00 (16)	V2—O6—V3	100.38 (17)
O7—V3—V5^{i}	83.42 (14)	V3—O7—V4^{i}	114.8 (2)
O8—V3—V5^{i}	32.94 (13)	V3—O8—V5^{i}	114.9 (2)
O5—V3—V5^{i}	124.28 (12)	V5—O10—V4	113.5 (2)
O6—V3—V5^{i}	86.64 (11)	V6—O12—V4	109.8 (2)
O13^{i}—V3—V5^{i}	48.52 (10)	V6—O13—V7	101.55 (16)
V2—V3—V5^{i}	119.30 (4)	V6—O13—V2	94.78 (15)
O9—V4—O10	103.9 (2)	V7—O13—V2	93.34 (14)
O9—V4—O7^{i}	102.1 (2)	V6—O13—V3^{i}	92.73 (14)
O10—V4—O7^{i}	91.83 (19)	V7—O13—V3^{i}	93.04 (14)
O9—V4—O3	102.0 (2)	V2—O13—V3^{i}	168.98 (19)
O10—V4—O3	91.66 (19)	V6—O13—V4	88.32 (14)
O7^{i}—V4—O3	154.04 (18)	V7—O13—V4	170.1 (2)
O9—V4—O12	99.6 (2)	V2—O13—V4	86.37 (13)
O10—V4—O12	156.56 (19)	V3^{i}—O13—V4	85.80 (13)
O7^{i}—V4—O12	83.15 (18)	V6—O13—V5	170.2 (2)
O3—V4—O12	83.47 (18)	V7—O13—V5	88.06 (14)
O9—V4—O13	173.7 (2)	V2—O13—V5	86.46 (13)
O10—V4—O13	82.46 (17)	V3^{i}—O13—V5	84.79 (13)
O7^{i}—V4—O13	77.84 (16)	V4—O13—V5	82.05 (13)
O3—V4—O13	77.14 (16)	V7—O14—V5	110.9 (2)
O12—V4—O13	74.10 (15)	Mn1—O1W—H1A	120 (9)
O9—V4—V5	137.1 (2)	Mn1—O1W—H1B	132 (6)
O10—V4—V5	33.24 (13)	H1A—O1W—H1B	107 (10)
O7^{i}—V4—V5	83.91 (14)	Mn1—O2W—H2A	119 (7)
O3—V4—V5	85.01 (14)	Mn1—O2W—H2B	116 (6)
O12—V4—V5	123.32 (13)	H2A—O2W—H2B	101 (9)
O13—V4—V5	49.23 (10)	Mn1—O3W—H3A	115 (8)
O9—V4—V6	130.8 (2)	Mn1—O3W—H3B	121 (5)
O10—V4—V6	125.37 (14)	H3A—O3W—H3B	107 (9)
O7^{i}—V4—V6	78.24 (13)	Mn1—O4W—H4A	115 (7)
O3—V4—V6	78.80 (13)	Mn1—O4W—H4B	108 (6)
O12—V4—V6	31.19 (12)	H4A—O4W—H4B	109 (9)
O13—V4—V6	42.92 (10)	Mn1—O5W—H5A	108 (10)
V5—V4—V6	92.13 (4)	Mn1—O5W—H5B	114 (9)
O9—V4—V2	134.20 (18)	H5A—O5W—H5B	126 (10)
O10—V4—V2	81.76 (13)	C10—N1—H1C	109.5
O7^{i}—V4—V2	123.37 (13)	C10—N1—H1D	109.5
O3—V4—V2	32.27 (13)	H1C—N1—H1D	109.5
O12—V4—V2	81.98 (12)	C10—N1—H1E	109.5
O13—V4—V2	45.54 (9)	H1C—N1—H1E	109.5
V5—V4—V2	60.90 (3)	H1D—N1—H1E	109.5
V6—V4—V2	61.87 (3)	N1—C10—C12	107.0 (6)
O11—V5—O10	104.4 (2)	N1—C10—C11	107.9 (5)
O11—V5—O8^{i}	102.2 (2)	C12—C10—C11	110.4 (6)
O10—V5—O8^{i}	92.89 (19)	N1—C10—C13	106.5 (6)
O11—V5—O4	102.3 (2)	C12—C10—C13	112.3 (7)

O10—V5—O4	90.75 (18)	C11—C10—C13	112.4 (6)
O8^{i}—V5—O4	153.41 (18)	O11A—C11—C10	109.8 (6)
O11—V5—O14	99.8 (2)	O11A—C11—H11B	109.7
O10—V5—O14	155.59 (19)	C10—C11—H11B	109.7
O8^{i}—V5—O14	84.32 (17)	O11A—C11—H11C	109.7
O4—V5—O14	81.60 (17)	C10—C11—H11C	109.7
O11—V5—O13	173.5 (2)	H11B—C11—H11C	108.2
O10—V5—O13	82.00 (17)	C11—O11A—H11A	109.5
O8^{i}—V5—O13	78.27 (16)	O12A—C12—C10	108.9 (6)
O4—V5—O13	76.18 (15)	O12A—C12—H12B	109.9
O14—V5—O13	73.68 (14)	C10—C12—H12B	109.9
O11—V5—V4	137.74 (19)	O12A—C12—H12C	109.9
O10—V5—V4	33.29 (14)	C10—C12—H12C	109.9
O8^{i}—V5—V4	84.94 (14)	H12B—C12—H12C	108.3
O4—V5—V4	83.76 (13)	C12—O12A—H12A	109.5
O14—V5—V4	122.39 (12)	O13A—C13—C10	110.4 (9)
O13—V5—V4	48.72 (10)	O13B—C13—C10	112.4 (11)
O11—V5—V7	130.60 (19)	O13A—C13—H13C	109.6
O10—V5—V7	124.92 (15)	C10—C13—H13C	109.6
O8^{i}—V5—V7	78.82 (13)	O13A—C13—H13D	109.6
O4—V5—V7	77.53 (12)	C10—C13—H13D	109.6
O14—V5—V7	30.77 (11)	H13C—C13—H13D	108.1
O13—V5—V7	42.93 (10)	O13B—C13—H13E	109.1
V4—V5—V7	91.65 (4)	C10—C13—H13E	109.1
O11—V5—V3^{i}	134.32 (17)	O13B—C13—H13F	109.1
O10—V5—V3^{i}	82.75 (14)	C10—C13—H13F	109.1
O8^{i}—V5—V3^{i}	32.17 (13)	H13E—C13—H13F	107.8
O4—V5—V3^{i}	122.87 (13)	C13—O13A—H13A	109.5
O14—V5—V3^{i}	82.10 (11)	C13—O13B—H13B	109.5
O13—V5—V3^{i}	46.69 (9)	H6A—O6WA—H6B	110 (4)
V4—V5—V3^{i}	60.92 (3)	H6C—O6WB—H6D	110 (4)
V7—V5—V3^{i}	61.69 (3)		

O1—V2—O3—V4	174.8 (2)	O14—V5—O10—V4	−6.4 (6)
O4—V2—O3—V4	70.3 (2)	O13—V5—O10—V4	−1.5 (2)
O6—V2—O3—V4	−34.8 (6)	V7—V5—O10—V4	−2.1 (3)
O5—V2—O3—V4	−85.9 (2)	V3^{i}—V5—O10—V4	45.64 (19)
O13—V2—O3—V4	−10.5 (2)	O9—V4—O10—V5	−178.9 (3)
V3—V2—O3—V4	−86.4 (2)	O7^{i}—V4—O10—V5	−76.0 (2)
O9—V4—O3—V2	−176.2 (3)	O3—V4—O10—V5	78.3 (2)
O10—V4—O3—V2	−71.7 (2)	O12—V4—O10—V5	1.0 (6)
O7^{i}—V4—O3—V2	25.9 (6)	O13—V4—O10—V5	1.5 (2)
O12—V4—O3—V2	85.3 (2)	V6—V4—O10—V5	0.9 (3)
O13—V4—O3—V2	10.2 (2)	V2—V4—O10—V5	47.49 (19)
V5—V4—O3—V2	−39.1 (2)	O12^{i}—V6—O12—V4	−179.3 (3)
V6—V4—O3—V2	54.1 (2)	O5—V6—O12—V4	80.9 (2)
O1—V2—O4—V5	−176.1 (2)	O5^{i}—V6—O12—V4	−80.2 (2)
O3—V2—O4—V5	−70.4 (2)	O13^{i}—V6—O12—V4	0.7 (9)

O6—V2—O4—V5	85.9 (2)	O13—V6—O12—V4	0.73 (19)
O5—V2—O4—V5	30.8 (6)	V4^{i}—V6—O12—V4	179.93 (3)
O13—V2—O4—V5	9.9 (2)	O14^{i}—V7—O14—V5	178.4 (3)
V3—V2—O4—V5	85.5 (2)	O6—V7—O14—V5	−82.4 (2)
V4—V2—O4—V5	−38.54 (19)	O6^{i}—V7—O14—V5	79.1 (2)
O2—V3—O7—V4^{i}	−174.8 (2)	O13—V7—O14—V5	−1.86 (18)
O8—V3—O7—V4^{i}	−69.9 (2)	O13^{i}—V7—O14—V5	−0.3 (8)
O5—V3—O7—V4^{i}	85.5 (2)	V5^{i}—V7—O14—V5	−179.85 (2)
O6—V3—O7—V4^{i}	28.6 (6)	N1—C10—C11—O11A	54.2 (7)
O13^{i}—V3—O7—V4^{i}	9.9 (2)	C12—C10—C11—O11A	170.8 (6)
V2—V3—O7—V4^{i}	84.1 (3)	C13—C10—C11—O11A	−63.0 (8)
V5^{i}—V3—O7—V4^{i}	−39.0 (2)	N1—C10—C12—O12A	−62.1 (8)
O2—V3—O8—V5^{i}	174.5 (2)	C11—C10—C12—O12A	−179.3 (6)
O7—V3—O8—V5^{i}	69.4 (2)	C13—C10—C12—O12A	54.4 (9)
O5—V3—O8—V5^{i}	−31.4 (6)	N1—C10—C13—O13A	−175.5 (8)
O6—V3—O8—V5^{i}	−85.5 (2)	C12—C10—C13—O13A	67.7 (10)
O13^{i}—V3—O8—V5^{i}	−9.9 (2)	C11—C10—C13—O13A	−57.5 (10)
V2—V3—O8—V5^{i}	−85.1 (2)	N1—C10—C13—O13B	−102.3 (14)
O11—V5—O10—V4	179.6 (2)	C12—C10—C13—O13B	140.9 (14)
O8^{i}—V5—O10—V4	76.2 (2)	C11—C10—C13—O13B	15.8 (15)
O4—V5—O10—V4	−77.4 (2)		

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O14^{ii}	0.70 (12)	2.01 (12)	2.703 (7)	167 (12)
O1*W*—H1*B*···O12^{iii}	0.70 (7)	2.04 (8)	2.727 (8)	169 (8)
O2*W*—H2*A*···O5^{iv}	0.60 (7)	2.12 (7)	2.716 (7)	172 (9)
O2*W*—H2*B*···O12*A*	0.87 (10)	2.01 (10)	2.858 (8)	164 (8)
O3*W*—H3*A*···O7^{iv}	0.70 (9)	1.94 (9)	2.636 (7)	176 (10)
O3*W*—H3*B*···O11*A*^{v}	0.88 (8)	1.91 (8)	2.752 (8)	160 (7)
O4*W*—H4*A*···O6^{vi}	0.82 (11)	1.90 (11)	2.708 (6)	167 (10)
O4*W*—H4*B*···O2*W*^{vi}	0.76 (9)	2.12 (9)	2.871 (7)	169 (9)
O5*W*—H5*A*···O8^{vi}	0.55 (11)	2.18 (11)	2.725 (10)	170 (16)
O5*W*—H5*B*···O13*A*^{v}	0.83 (14)	2.12 (13)	2.699 (12)	127 (12)
O5*W*—H5*B*···O13*B*^{v}	0.83 (14)	1.95 (14)	2.77 (2)	168 (13)
N1—H1*C*···O3*W*^{vi}	0.89	2.03	2.898 (7)	164
N1—H1*D*···O2	0.89	2.31	3.032 (7)	138
N1—H1*D*···O4*W*	0.89	2.45	3.105 (7)	130
N1—H1*E*···O4^{vi}	0.89	1.91	2.787 (6)	166
C11—H11*C*···O11^{vi}	0.97	2.46	3.392 (9)	160
O11*A*—H11*A*···O6*WA*^{vi}	0.82	1.96	2.758 (12)	166
O12*A*—H12*A*···O3^{iv}	0.82	1.94	2.756 (7)	174
C13—H13*E*···O2	0.97	2.40	3.280 (10)	151
O13*B*—H13*B*···O6*WB*^{vii}	0.77	1.92	2.60 (2)	148
O6*WA*—H6*A*···O3	0.82 (2)	2.23 (9)	2.966 (9)	150 (15)

O6*WA*—H6*B*···O10^{viii}	0.82 (2)	2.16 (5)	2.952 (10)	165 (17)
O6*WB*—H6*C*···O3	0.82 (2)	2.03 (13)	2.802 (17)	156 (29)
O6*WB*—H6*D*···O10^{viii}	0.82 (2)	1.93 (8)	2.720 (19)	161 (24)

Symmetry codes: (ii) x+1/2, y+1/2, z; (iii) x+1/2, y−1/2, z; (iv) −x+3/2, y−1/2, −z+1/2; (v) x, −y+1, z−1/2; (vi) −x+3/2, y+1/2, −z+1/2; (vii) x, −y+1, z+1/2; (viii) −x+1, −y+1, −z.