

Octasodium hexatungstomanganate(IV) octadecahydrate

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The title compound, $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$, exhibits a structure with six WO_6 octahedral edge-sharing units surrounding a central centrosymmetric MnO_6 octahedron, with all metal atoms in a common plane. There are three unique Mn—O distances of 1.903 (7), 1.905 (7) and 1.941 (7) Å [average 1.916 (17) Å], while the average W—O distances are 2.17 (4), 1.938 (8) and 1.749 (12) Å for three-, two- and one-coordinate O atoms, respectively.

Comment

As part of our studies into the structures and range of heteroatoms found in heteropolyoxomolybdates and -tungstates, we have examined the structure of the title compound, $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$.

The structure consists of Na^+ cations, an $[\text{MnW}_6\text{O}_{24}]^{8-}$ anion and water molecules of crystallization. The geometry of the anion is based on the standard Anderson structure (Anderson, 1937), with six WO_6 octahedral edge-sharing units surrounding the central MnO_6 octahedron and with all metal atoms essentially in a common plane (the maximum deviation of a W atom from the least-squares plane is 0.028 Å).

A view of the anion is shown in Fig. 1. The central Mn^{IV} atom is coordinated to six O atoms in a slightly distorted octahedral arrangement. There are three crystallographically unique Mn—O bonds [1.903 (7), 1.905 (7) and 1.941 (7) Å], two of which are significantly shorter than the third by 2.2σ . These bond distances may be compared with that found in $\text{Na}_2\text{K}_6[\text{MnW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ [one independent distance of 1.943 (7) Å; Sergienko *et al.*, 1979] and with those in $\text{K}_6[\text{MnMo}_9\text{O}_{32}] \cdot 6\text{H}_2\text{O}$ [1.884 (6) Å; Dunne *et al.*, 1992] and $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 6\text{H}_2\text{O}$ [1.897 (3) Å; Stratemeier *et al.*, 1992].

The Mn—O distances in $[\text{MnMo}_9\text{O}_{32}]^{6-}$ are shorter than in $[\text{MnW}_6\text{O}_{24}]^{8-}$, which is related to the extent of polymerization of the two types of polyoxometalate cage, while the differences in the two Anderson-based structures are associated with the immediate environments surrounding the O atoms of

the central MnO_6 unit. Thus, the bond valences (Brown & Altermatt, 1985) of O112, O113 and O123 are 1.76 (5), 1.74 (5) and 1.48 (5), respectively, compared with that of the oxygen (all central O atoms are equivalent) in $\text{Na}_2\text{K}_6[\text{MnW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$, which is 1.67 (5). All are somewhat less than the expected value of 2, and indicate close contacts to neighbouring atoms in each case. For $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$, these are to water molecules, based on the short O...O distances (2.70–2.82 Å), while in $\text{Na}_2\text{K}_6[\text{MnW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$, the interaction is to the (unique) K^+ ion.

Although the distances to the H atoms of the adjacent water molecules are unknown, the H...O bond valence—O...O distance correlation plot provided by Brown & Altermatt (1985) may be used to calculate the contribution for these types of interactions to the bond-valence sums for the central O atoms of the MnO_6 unit in the present structure. The bond valences increase to 1.94 (5), 1.94 (5) and 1.67 (5) for O112, O113 and O123, respectively. For the central O atom in $\text{Na}_2\text{K}_6[\text{MnW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$, inclusion of the contribution from the $\text{K}^+ \cdots \text{O}$ interaction (2.782 Å) gives a bond valence of 1.84 (6). Of all such interactions in the two structures, the only really low value is to O123 in $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$, but this may simply result from the packing of the water molecules and Na^+ ions around the anion, such that no further strong contacts can be made [the next shortest distance is O123...OW6 of 2.764 (13) Å]. Interestingly, O123 has the only interaction of all the centrally located O atoms with an Na^+ ion [3.365 (9) Å], although any contribution to the bond-valence sum from this ion is negligible. Thus, it appears that in Anderson-based structures that do not contain protonated centrally located O atoms, such as in $(\text{NH}_4)_4[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (Nolan *et al.*, 1996), strong interactions with adjacent water molecules can have a significant effect on the

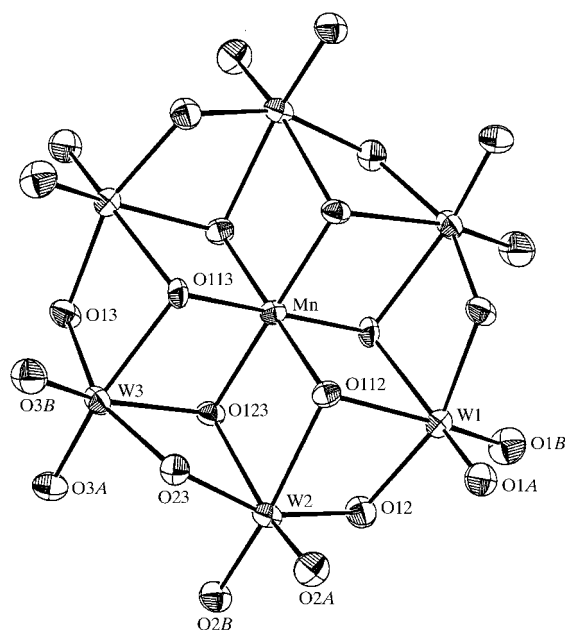


Figure 1

The anion of $\text{Na}_8[\text{MnW}_6\text{O}_{24}] \cdot 18\text{H}_2\text{O}$ with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

heteroatom–oxygen distances in the XO_6 unit (X = heteroatom).

In the present structure, the O–Mn–O angles vary from 82.3 (3) to 97.7 (3)°, indicating the extent of angular distortion around the Mn^{IV} atom, and they are similar to the range of 82.6 (3)–97.4 (3)° found in Na₂K₆[MnW₆O₂₄]·12H₂O. The W atoms are all six-coordinate, although the distortion from octahedral symmetry is extensive. Each W atom is coordinated twice to three-coordinate O atoms, twice to two-coordinate O atoms and twice to terminal O atoms. The W–O bond lengths decrease with decreasing coordination of the O atom. The average Mn···W and W···W distances are 3.204 (19) and 3.171 (2) Å, respectively. All cation–anion distances are longer than 2.339 Å and all anion–water distances are longer than 2.70 Å. Although no H atoms were located, the short anion–water distances provide evidence for hydrogen bonding between the anion and water molecules.

Experimental

A solution containing Na₂WO₄·2H₂O (19.8 g, 0.060 mol) in water (75 ml) was adjusted to pH 4.8 with concentrated nitric acid, and a solution containing MnSO₄·H₂O (1.70 g, 0.010 mol, 20 ml) was added dropwise. The resulting pale-yellow solution formed a yellow precipitate after about 10 min of stirring, which redissolved on heating. The solution was heated to boiling and solid Na₂S₂O₈ (4.80 g, 0.020 mol) was added with constant stirring. The solution turned red-brown slowly, indicating oxidation of Mn^{II} to Mn^{IV}. Boiling was continued until the evolution of oxygen ceased, by which time the solution was a dark red–brown colour. The solution was filtered while still hot and the filtrate placed in a 250 ml beaker, covered with a watchglass and allowed to remain undisturbed at room temperature. Over a period of several weeks, MnO₂ initially precipitated and the solution was decanted several times. Eventually, red–brown crystals formed, which were filtered off, washed with ice-cold water and dried (10.25 g, 50% yield). Spectroscopic analysis: UV–vis (water, pH 5.0): λ_{max} 480 nm, ε 380 dm³ mol⁻¹ cm⁻¹; IR (KBr disk, cm⁻¹): 912 (s) (W=O stretching), 863 (s), 700 (s) (W–O–W and W–O–Mn stretching).

Crystal data

Na₈[MnW₆O₂₄]·18H₂O
M_r = 2050.22
 Monoclinic, *P*2₁/*c*
a = 11.686 (12) Å
b = 11.671 (6) Å
c = 16.667 (18) Å
 β = 120.80 (4)°
V = 1952.6 (31) Å³
Z = 2

D_x = 3.487 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 10 reflections
 θ = 10–11°
 μ = 18.089 mm⁻¹
T = 293 (2) K
 Plate, red–brown
 0.20 × 0.18 × 0.03 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 θ/2θ scans
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.06, *T_{max}* = 0.46
 3423 measured reflections
 3423 independent reflections

3017 reflections with *I* > 2σ(*I*)
 θ_{max} = 24.99°
h = –13 → 11
k = 0 → 13
l = 0 → 19
 1 standard reflection
 frequency: 30 min
 intensity decay: <1%

Table 1
 Selected bond lengths (Å).

Mn–O112	1.903 (7)	W2–O12	1.930 (8)
Mn–O113	1.905 (7)	W2–O23	1.949 (7)
Mn–O123	1.941 (7)	W2–O112	2.134 (8)
W1–O1B	1.739 (8)	W2–O123	2.208 (7)
W1–O1A	1.768 (8)	W3–O3A	1.737 (8)
W1–O13 ⁱ	1.929 (8)	W3–O3B	1.747 (8)
W1–O12	1.947 (8)	W3–O13	1.931 (8)
W1–O112	2.150 (7)	W3–O23	1.944 (8)
W1–O113 ⁱ	2.153 (7)	W3–O113	2.142 (7)
W2–O2A	1.739 (8)	W3–O123	2.239 (7)
W2–O2B	1.761 (8)		

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

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.038
wR (*F*²) = 0.120
S = 0.963
 3423 reflections
 259 parameters

H-atom parameters undefined
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.185
 Δρ_{max} = 2.46 e Å⁻³
 Δρ_{min} = –2.35 e Å⁻³

There appeared to be some positional disorder associated with the Na3 and Na4 cation positions, based on residual peaks in the Fourier difference map, but attempts to locate separate atoms in reasonable locations failed to produce any further satisfactory refinement. The maximum peak and minimum trough were located close to the W atoms, but not in chemically significant positions.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local software (University of New South Wales); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1280). Services for accessing these data are described at the back of the journal.

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