Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.642$, $T_{\max} = 0.922$
2501 measured reflections
1790 independent reflections
1279 observed reflections [$F > 4\sigma(F)$]
$R_{\rm int} = 0.0405$
$\theta_{\max} = 30.0°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 12$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.037$
$wR = 0.034$
$S = 1.24$
1279 reflections
89 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -0.69$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 0.00092 (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mn	1/2	1/2	1/2	0.010 (1)
V(1)	0.8332 (1)	0.7876 (1)	0.6208 (1)	0.010 (1)
V(2)	0.6988 (1)	0.9419 (1)	0.2395 (1)	0.012 (1)
K	0.1413 (2)	0.8021 (1)	0.4072 (1)	0.022 (1)
O(1)	0.8158 (5)	0.9092 (4)	0.4559 (4)	0.018 (1)
O(2)	0.8492 (5)	0.8832 (4)	0.7876 (4)	0.020 (1)
O(3)	0.6613 (5)	0.6832 (4)	0.5864 (4)	0.020 (1)
O(5)	0.8339 (4)	0.9254 (4)	0.1349 (4)	0.019 (1)
O(4)	1.0239 (5)	0.6838 (4)	0.6558 (4)	0.027 (1)
O(6)	0.6275 (6)	1.1057 (4)	0.2269 (5)	0.032 (2)

Table 2. *Selected geometric parameters (Å, °)*

Mn—O(3)	2.118 (4)	V(2)—O(4$^{\rm iii}$)	1.792 (4)
Mn—O(2$^{\rm i}$)	2.128 (3)	K—O(6$^{\rm iv}$)	2.780 (4)
Mn—O(5$^{\rm ii}$)	2.175 (4)	K—O(1$^{\rm v}$)	2.994 (4)
V(1)—O(1)	1.781 (3)	K—O(1$^{\rm vi}$)	2.887 (4)
V(1)—O(2)	1.657 (4)	K—O(2$^{\rm iii}$)	2.837 (4)
V(1)—O(3)	1.645 (4)	K—O(3$^{\rm iii}$)	2.836 (4)
V(1)—O(4)	1.765 (4)	K—O(5$^{\rm vii}$)	2.944 (3)
V(2)—O(1)	1.817 (3)	K—O(5$^{\rm v}$)	3.026 (3)
V(2)—O(5)	1.654 (4)	K—O(4$^{\rm v}$)	2.848 (4)
V(2)—O(6)	1.610 (4)		
O(3)—Mn—O(2$^{\rm i}$)	89.4 (1)	O(2)—V(1)—O(3)	106.3 (2)
O(3)—Mn—O(2$^{\rm iii}$)	90.6 (1)	O(1)—V(1)—O(4)	107.8 (2)
O(2$^{\rm i}$)—Mn—O(2$^{\rm iii}$)	180.0 (1)	O(2)—V(1)—O(4)	109.5 (2)
O(3)—Mn—O(3$^{\rm viii}$)	180.0 (1)	O(3)—V(1)—O(4)	111.3 (2)
O(3)—Mn—O(5$^{\rm ii}$)	90.8 (1)	O(1)—V(2)—O(5)	109.3 (2)
O(2$^{\rm i}$)—Mn—O(5$^{\rm ii}$)	91.0 (1)	O(1)—V(2)—O(6)	106.2 (2)
O(2$^{\rm iii}$)—Mn—O(5$^{\rm ii}$)	89.0 (1)	O(5)—V(2)—O(6)	110.0 (2)
O(3)—Mn—O(5$^{\rm vii}$)	89.2 (1)	O(1)—V(2)—O(4$^{\rm iii}$)	112.4 (2)
O(5$^{\rm ii}$)—Mn—O(5$^{\rm vii}$)	180.0 (1)	O(5)—V(2)—O(4$^{\rm iii}$)	108.0 (2)
O(1)—V(1)—O(2)	108.8 (2)	O(6)—V(2)—O(4$^{\rm iii}$)	111.0 (2)
O(1)—V(1)—O(3)	113.0 (2)		

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SHELXTL-Plus XPREP* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus XS*. Program(s) used to refine structure: *SHELXTL-Plus XLS*. Molecular graphics: *SHELXTL-Plus XP*. Software used to prepare material for publication: *SHELXTL-Plus XPUB*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$K_2Mn_3(OH)_2(VO_4)_2$, a New Two-Dimensional Potassium Manganese(II) Hydroxyvanadate

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Abstract

Trimanganese(II) dipotassium bis(hydroxide) bis(tetraoxovanadate), $K_2Mn_3(OH)_2(VO_4)_2$, has a layered structure. The $[Mn_3(OH)_2(VO_4)_2]_n^{2n-}$ layers comprise CdI_2-like planes of $MnO_4(OH)_2$ octahedra with 1/4 Mn vacancies to which VO_4 tetrahedra are linked on both sides *via* three vertices; the fourth vertex points into the interlayer space where the K^+ ions are situated.

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Comment

Two potassium manganese vanadates have already been reported: $K_{10}Mn_2V_{22}O_{64}.20H_2O$ and $K_5H_3Mn_3V_{12}O_{40}.8H_2O$ (Ichida, Nagai, Sasaki & Pope, 1989). Both are heteropolyvanadates containing Mn^{IV} cations. The title compound, $K_2Mn_3(OH)_2(VO_4)_2$, was prepared in a basic medium. It has a layered structure built up from $MnO_4(OH)_2$ octahedra and VO_4 tetrahedra (Fig. 1). Each $MnO_4(OH)_2$ octahedron shares four edges with four other octahedra in the same plane thus forming CdI_2-like layers with 1/4 Mn vacancies. Each hydroxyl O atom [O(1)] is shared by one Mn(1) and two Mn(2) cations. The VO_4 tetrahedra are linked to these $[Mn_3(vacancy)O_6(OH)_2]_n$ layers on both sides of the Mn vacancies *via* three O atoms, leading to $[Mn_3(OH)_2(VO_4)_2]_n^{2n-}$ layers. The fourth vertex points into the interlayer space where the K^+ ions are situated (Fig. 2).

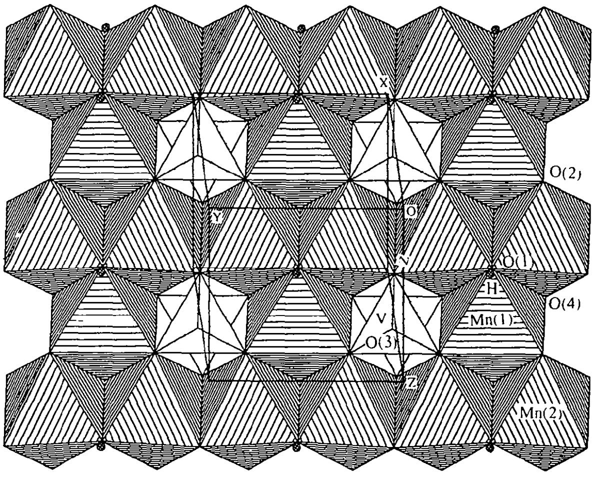

Fig. 1. Perspective [100]* view of an $[Mn_3(OH)_2(VO_4)_2]_n^{2n-}$ layer.

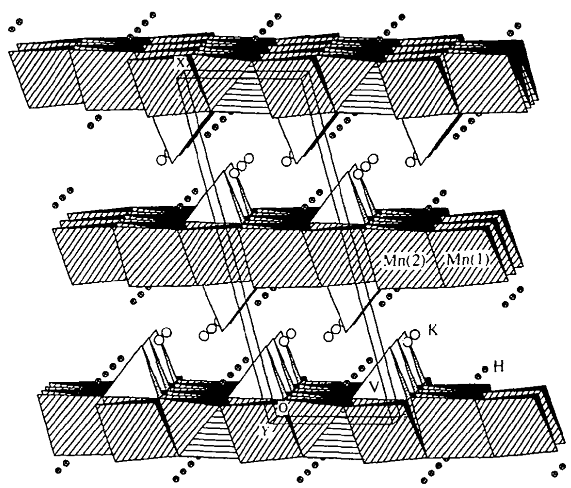

Fig. 2. Perspective [010] view of the layered $K_2Mn_3(OH)_2(VO_4)_2$ structure.

Each K^+ ion is surrounded by seven O atoms with K—O distances ranging from 2.705 (4) to 3.140 (1) Å (Table 2). The distances between Mn and the triply bridging hydroxyl O atom [O(1)] are relatively short compared with other Mn—O distances. The shortest V—O distance is to the terminal O atom; this O atom is not bonded to Mn and is only weakly bonded to K. The Mn—O and V—O bonds are unexceptional and correspond well with those typically observed in Mn^{II} and V^{V} oxides.

Bond-valence sum calculations (Brese & O'Keeffe, 1991; Brown & Altermatt, 1985) confirm the oxidation state assignments and allow the identification of O(1) as the hydroxyl O atom. In the difference electron-density map, a peak 0.993 (2) Å from O(1) was observed and assigned to an H atom. The O(1)—H bond points toward the terminal V—O(3) bond in an adjacent layer, leading to a weak hydrogen bond of 1.869 (3) Å (0.19 v.u.) and an O(1)—H···O(3) angle of 161.7 (2)°. O(3) is surrounded by four nearly coplanar K^+ cations, which contribute 0.49 v.u. to the O(3) bond-valence sum (2.07 v.u.).

Experimental

Single crystals of $K_2Mn_3(OH)_2(VO_4)_2$ were obtained by heating a mixture of $H_2Mn_4O_9.xH_2O$ (0.207 g, 0.5 mmol), V_2O_5 (0.364 g, 2.0 mmol), $K_2S_2O_8$ (0.135 g, 0.5 mmol), 5 ml 1 *M* KOH and 5 ml MeOH in an autoclave at 453 K (autogenous pressure) for one week.

Crystal data

$K_2Mn_3(OH)_2(VO_4)_2$
$M_r = 506.9$
Monoclinic
$C2/m$
$a = 15.204\ (2)$ Å
$b = 6.1593\ (5)$ Å
$c = 5.3998\ (4)$ Å
$\beta = 105.401\ (9)°$
$V = 487.54\ (8)$ Å^3
$Z = 2$
$D_x = 3.453$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.19–15.39°$
$\mu = 6.52$ mm^{-1}
$T = 293$ K
Parallelepiped
0.18 × 0.08 × 0.04 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan
$T_{min} = 0.844$, $T_{max} = 0.995$
2217 measured reflections
1529 independent reflections
1296 observed reflections [$F > 4\sigma(F)$]

$R_{int} = 0.016$
$\theta_{max} = 40.0°$
$h = -27 \rightarrow 27$
$k = -1 \rightarrow 11$
$l = -1 \rightarrow 9$
3 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.040$

$\Delta\rho_{max} = 1.78$ e Å^{-3}
$\Delta\rho_{min} = -1.49$ e Å^{-3}

$wR = 0.046$
$S = 1.93$
1296 reflections
50 parameters
H atom fixed but included in calculations
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$

Extinction correction: Larson (1970)
Extinction coefficient: 0.0056 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å²)

$U_{\rm iso}$ for H atom, $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Mn(1)	0	0	0	0.009 (1)
Mn(2)	0	0.2644 (1)	1/2	0.009 (1)
V	0.3793 (1)	0	0.9076 (1)	0.006 (1)
K	0.2622 (1)	1/2	0.7047 (2)	0.017 (1)
O(1)	0.0724 (2)	0	−0.2817 (6)	0.009 (1)
O(2)	0.4145 (1)	0.2318 (3)	0.7767 (4)	0.010 (1)
O(3)	0.2648 (2)	0	0.8200 (6)	0.015 (1)
O(4)	0.4149 (2)	0	0.2436 (6)	0.009 (1)
H	0.1396	0	0.7920	0.050

Table 2. *Selected geometric parameters* (Å, °)

Mn(1)—O(1)	2.101 (3)	K—O(2)	2.786 (2)
Mn(1)—O($2^{\rm i}$)	2.245 (2)	K—O(3)	3.140 (1)
Mn(2)—O($1^{\rm ii}$)	2.136 (2)	K—O($2^{\rm vi}$)	2.786 (2)
Mn(2)—O($2^{\rm iii}$)	2.226 (2)	K—O($3^{\rm vii}$)	3.140 (1)
Mn(2)—O($4^{\rm iv}$)	2.178 (2)	K—O($3^{\rm viii}$)	2.705 (4)
V—O(2)	1.739 (2)	K—O($3^{\rm iii}$)	2.753 (3)
V—O(3)	1.678 (3)	K—O($4^{\rm iii}$)	2.781 (3)
V—O($2^{\rm v}$)	1.739 (2)	O(1)—$H^{\rm ix}$	0.993 (2)
V—O($4^{\rm ii}$)	1.751 (3)		
O(1)—Mn(1)—O($1^{\rm x}$)	180.0 (1)	O($1^{\rm ii}$)—Mn(2)—O($4^{\rm iv}$)	172.1 (1)
O(1)—Mn(1)—O($2^{\rm i}$)	87.2 (1)	O($1^{\rm x}$)—Mn(2)—O($4^{\rm iv}$)	91.4 (1)
O($1^{\rm x}$)—Mn(1)—O($2^{\rm i}$)	92.8 (1)	O($2^{\rm iii}$)—Mn(2)—O($4^{\rm iv}$)	85.4 (1)
O($2^{\rm i}$)—Mn(1)—O($2^{\rm iii}$)	180.0 (1)	O($2^{\rm xii}$)—Mn(2)—O($4^{\rm iv}$)	93.8 (1)
O($2^{\rm i}$)—Mn(1)—O($2^{\rm xi}$)	85.2 (1)	O($4^{\rm iv}$)—Mn(2)—O($4^{\rm iii}$)	96.4 (1)
O($2^{\rm iii}$)—Mn(1)—O($2^{\rm xi}$)	94.8 (1)	O(2)—V—O(3)	107.1 (1)
O($1^{\rm ii}$)—Mn(2)—O($1^{\rm x}$)	80.7 (1)	O(2)—V—O($2^{\rm v}$)	110.3 (2)
O($1^{\rm ii}$)—Mn(2)—O($2^{\rm iii}$)	94.1 (1)	O(2)—V—O($4^{\rm ii}$)	112.2 (1)
O($1^{\rm x}$)—Mn(2)—O($2^{\rm iii}$)	86.8 (1)	O(3)—V—O($4^{\rm ii}$)	107.7 (2)
O($2^{\rm iii}$)—Mn(2)—O($2^{\rm xii}$)	178.8 (1)		

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

Data collection: *CAD*-4 *software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *software*. Data reduction: *SHELXTL-Plus XPREP* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus XS*. Program(s) used to refine structure: *SHELXTL-Plus XLS*. Molecular graphics: *SHELXTL-Plus XP*. Software used to prepare material for publication: *SHELXTL-Plus XPUB*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tin(II) Oxyhydroxide by X-ray Powder Diffraction

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Abstract

The structure of tin(II) oxide hydroxide, $Sn_6O_4(OH)_4$, has been refined by Rietveld analysis of X-ray powder diffraction data. Atomic parameters based on the isostructural lead analogue were used in the starting model. The structure was refined in the tetragonal space group $P\bar{4}2_1c$ with $a = 7.9268 (4)$ and $c = 9.1025 (5)$ Å. The title compound forms clusters of $Sn_6O_4(OH)_4$ with the Sn atoms in distorted tetragonal pyramidal coordination geometries. Each Sn atom is coordinated to two bridging oxide O and two bridging hydroxy O atoms. The JCPDS file number for $Sn_6O_4(OH)_4$ is 46-1486.

Comment

Tin(II) oxyhydroxide is readily precipitated from mildly alkaline aqueous solutions of stannous salts. Preparation of single crystals of this compound has proved particularly difficult. A single-crystal study has been performed (Howie & Moser, 1968, 1973) which identified a tetragonal structure (space group *P*4/*mnc*) and the presence of discrete $Sn_6O_4(OH)_4$ clusters; however, no atomic coordinates were published. The structure of $Pb_6O_4(OH)_4$ has been determined by powder neutron diffraction (Hill, 1985) and similarities in the X-ray powder diffraction data for these two compounds indicate that they are isostructural. Structure refinement of $Sn_6O_4(OH)_4$ has been carried out as part of a gen-