Leduc, L., Perrin, A., Sergent, M., Le Traon, F., Pilet, J. C. & Le Traon, A. (1985). *Mater. Lett.* **3**, 209–215.
Long, J. R., Williamson, A. S. & Holm, R. H. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 226–229.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Opalovskii, A. A., Fedorov, V. E., Lobkov, E. U. & Erenburg, B. G. (1971). *Russ. J. Inorg. Chem. (Engl. Transl.)*, **16**, 1685.
Perrin, A. & Sergent, M. (1988). *New J. Chem.* **12**, 337–356.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Yaghi, O. M., Scott, M. J. & Holm, R. H. (1992). *Inorg. Chem.* **31**, 4778–4784.

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$K_2Mn(VO_3)_4$, a New Three-Dimensional Potassium Manganese(II) Polyvanadate

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Abstract

The structure of potassium manganese(II) polyvanadate, $K_2Mn(VO_3)_4$, is composed of VO_4 tetrahedra and MnO_6 octahedra. Parallel zigzag polyvanadate $(VO_3)_n^{n-}$ chains of corner-sharing VO_4 tetrahedra are cross-linked by separate MnO_6 octahedra to form a three-dimensional structure with K^+ cations situated in void space.

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 potassium manganese(II) polyvanadate $K_2Mn(VO_3)_4$ has been prepared in a basic medium. Its structure is composed of VO_4 tetrahedra and MnO_6 octahedra (Fig. 1). Each VO_4 tetrahedron shares two of its vertices with two VO_4 tetrahedra to form parallel zigzag $(VO_3)_n^{n-}$ chains of alternating V(1)O_4 and V(2)O_4 tetrahedra, running along [101]. Within a chain, each V(1)O_4 tetrahedron shares its two remaining vertices with two MnO_6 octahedra, whereas each V(2)O_4 tetrahedron shares only one vertex with another MnO_6 octahedron. The fourth O atom, O(6), as yet unshared, of the V(2)O_4 tetrahedron points toward a cavity where a K^+ cation is situated. Each MnO_6 octahedron is then connected to six different tetrahedra [four V(1)O_4 tetrahedra and two V(2)O_4 tetrahedra] which belong to four different chains. Each K^+ cation is surrounded by eight O atoms with K—O distances ranging from 2.780 (4) to 3.026 (3) Å. The Mn—O and V—O bonds are unexceptional and correspond well with those typically observed in Mn^{II} and V^V oxides. The shortest V—O distance involves the terminal O atom, O(6), *i.e.* not bonded to Mn, but leading to the shortest K—O distance. Bond-valence sum calculations (Brese & O'Keeffe, 1991; Brown & Altermatt, 1985) confirm oxidation-state assignments.

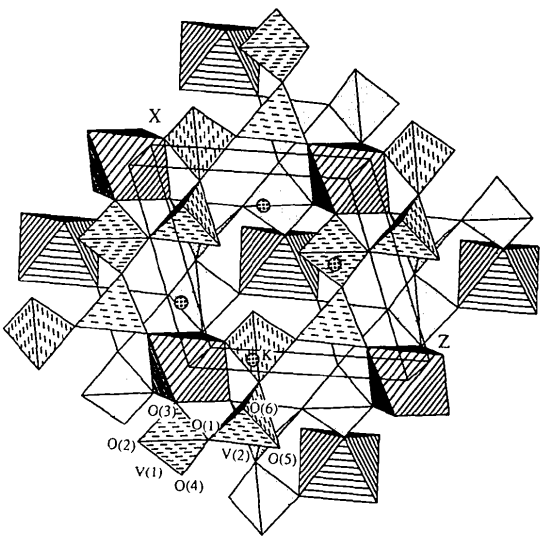

Fig. 1. Polyhedral representation of $K_2Mn(VO_3)_4$, viewed down the *b* axis.

Experimental

Single crystals of $K_2Mn(VO_3)_4$ 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), 9.5 ml of 1*M* KOH and 0.5 ml of acetone in an autoclave at 453 K (autogenous pressure) for one week.

Crystal data

$K_2Mn(VO_3)_4$
M_r = 528.9
Monoclinic
$P2_1/n$
a = 8.1678 (9) Å
b = 9.226 (1) Å
c = 8.6395 (8) Å
β = 109.678 (8)°
V = 613.0 (1) Å^3
Z = 2
D_x = 2.865 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.3–25.1°
μ = 4.668 mm^{-1}
T = 293 K
Plate
0.16 × 0.11 × 0.02 mm
Red

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_{int} = 0.0405
θ_{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)*

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

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

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Ichida, H., Nagai, K. N., Sasaki, Y. & Pope, M. T. (1989). *J. Am. Chem. Soc.* **111**, 586–591.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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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.