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The Structure of Heptapotassium Tridecavanadomanganate (IV) Octadecahydrate, $K_7[MnV_{13}O_{38}]\cdot18H_2O$

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M_r=1923.1, tetragonal, I4/mmm, a=11.366(2), c=19.638(6)Å, V=2537(1) $Å^3$, Z=2,D_x=2.52 g cm^{-3}, MoKα, λ =0.71069 Å, μ =3.12 mm^{-1}, F(000)=1882, R=0.097 for 566 independent reflections. The crystal of $K_7[MnV_{13}O_{38}]\cdot18H_2O$ was found to be isomorphous to that of $K_7[NiV_{13}O_{38}]\cdot18H_2O$. Corresponding interatomic distances between the two anions are essentially equal to each other. V-O bond distances range from 1.59 to 2.38 Å. One of the three K^+ ions is tightly surrounded by 6 - 8 O atoms of the polyanions.

Only few structures of heteropolyvanadates have been revealed so far,1) because there was smaller regard for vanadates than molybdates and tungstates. The syntheses of heptapotassium tridecavanadomanganate(IV) and nickelate(IV) were first reported by Flynn and Pope2) which was followed by the paper about heteropolyvanadomanganates(IV) with Mn:V=1:11 and 1:4.3) The structure of $K_7[NiV_{13}O_{38}]\cdot18H_2O$ was determined by Kobayashi and Sasaki.4) This communication reports the structure of its Mn(IV) analogue. It has been found that the structure is essentially identical with that of the tridecavanadonickelate, and more detailed information has been obtained about the distribution of the potassium cations and water molecules in the crystal.

The fragile orange crystals have been prepared by the method reported by Flynn and Pope.2) A single crystal which has dimensions 0.1 x 0.2 x 0.3 mm^3 was mounted upon a Rigaku automated four-circle diffractometer. Reflection data were collected by monochromated Mo Kα(λ=0.71069 Å), using ω -2θ scan mode up to 2θ=60° ($0\le h\le15$, $0\le k\le15$, $0\le \ell\le27$). No absorption corrections were made. With $|F|\ge3\sigma(F)$, 566 averaged independent reflections were used for the structure analysis. Number of water molecules was determined by elemental analysis.

Table 1. Positional parameters (x10^4 for Mn and V, and x 10^3 for others) isotropic thermal parameters ($Å^2$)(B_{eq}7)) x 10^2 for Mn and V and B_{iso} x 10 for others), equivalent points, occupancies and multiplicities

Atom	X	Y	Z	B_{eq} or B_{iso}	Equipoint	Occupancy	Multiplicity
Mn1	0(0)	0(0)	0(0)	166(13)	2(a)	1	1/16
V 1	1990(2)	0(0)	1046(1)	212(5)	16(n)	1	1/2
V 2	2062(5)	2062(5)	0(0)	202(10)	8(h)	3/4	3/16
V 3	0(0)	0(0)	2131(3)	270(12)	4(e)	1	1/8
O 1	0(0)	170(1)	0(0)	18(3)	8(i)	1	1/4
O 2	350(1)	189(1)	0(0)	31(4)	16(l)	3/4	3/8
O 3	164(1)	164(1)	93(0)	23(2)	16(m)	1	1/2
O 4	339(1)	0(0)	106(1)	29(3)	16(n)	1	1/2
O 5	0(0)	0(0)	91(1)	16(4)	4(e)	1	1/8
O 6	162(1)	0(0)	192(1)	27(2)	16(n)	1	1/2
O 7	0(0)	0(0)	297(1)	39(7)	4(e)	1	1/8
K(1)	500(0)	0(0)	0(0)	35(2)	8(i)	1/2	1/8
K(2)	288(4)	288(4)	189(2)	189(11)	16(m)	3/8	3/16
K(3)	500(0)	343(4)	78(2)	169(14)	32(o)	1/8	1/8
Aq(1)	500(0)	153(3)	217(2)	161(12)	32(o)	3/8	3/8
Aq(2)	500(0)	260(5)	135(3)	239(22)	32(o)	3/8	3/8

The structure was solved by the use of the Patterson function, and atomic parameters were refined anisotropically by means of block diagonal least-squares methods. During the course of the refinement, the temperature factors of V(2) and O(2) atoms were found to be too large compared with the other atoms. Their occupancies were refined to be ca.3/4. Assuming the polyanion with symmetry C_{2v} to be located at D_{4h} site, their occupancies were fixed to be 3/4 in the subsequent refinement. The atoms K(1), K(2), K(3), the oxygen atoms of the water molecules Aq(1) and Aq(2) have 4,8,16,16,16 sites respectively in the unit cell. Their site occupancies were also refined and were found to be 1/2, 3/8, 1/8, 3/8, and 3/8 respectively giving the foumula $K_7[MnV_{13}O_{38}]\cdot 12H_2O$. It was not attempted to locate the other 6 water molecules, which may have smaller occupancies. Final refinement gave R and R_w values of 0.097 and 0.110, with a weighting scheme, $w^{-1}= \sigma^2(Fo) + (0.04F_o)^2$. Complex atomic scattering factors of the all the atoms

Table 2. Bond lengths (Å) in $[MnV_{13}O_{38}]^{7-}$ anion

Mn-O(1)	1.931(14)
-O(5)	1.802(19)
V(1)-O(1)	2.078(4)
-O(3)	1.920(3)
-O(4)	1.591(12)
-O(5)	2.275(3)
-O(6)	1.769(12)
V(2)-O(1)	2.378(8)
-O(2)	1.648(15)
-O(3)	1.955(10)
V(3)-O(5)	2.379(20)
-O(6)	1.880(12)
-O(7)	1.662(30)

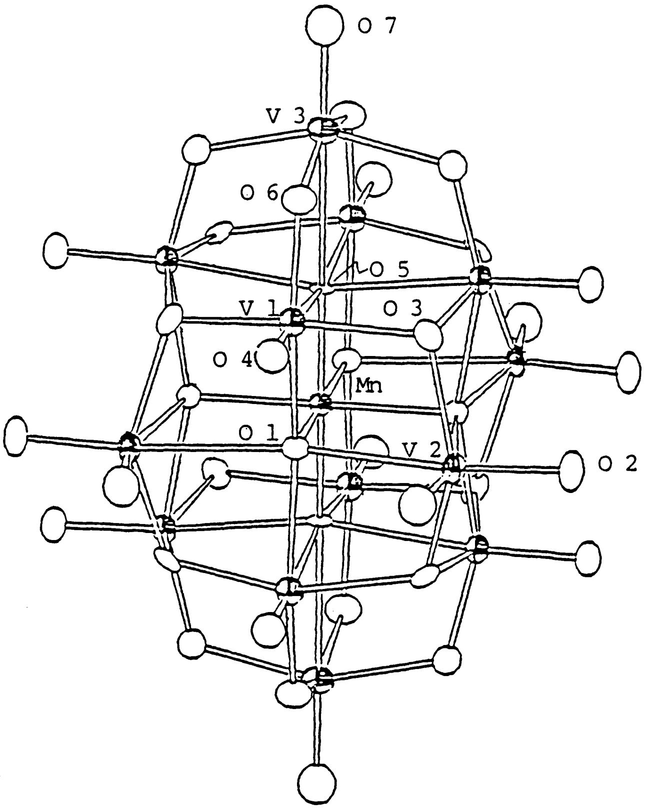

Fig.1. The structure of $[MnV_{13}O_{38}]^{7-}$ anion.

were taken from International Tables for X-ray Crystallography.5) All calculations were carried out on the HITAC M-280H computer at the Computer Centre of the University of Tokyo, using UNICS III.6) Final atomic parameters are listed in Table 1.

Figure 1 shows the molecular structure of $[MnV_{13}O_{38}]^{7-}$ anion, which takes C_{2v} symmetry. Metal-oxygen bond distances are given in Table 2. These are essentially equal to the corresponding ones found in the analogous vanadonickelate anion. Despite of not accurate values because of the random orientation of the molecule, these bond lengths reflect the coordination number of each O atom. As more coordination number of O atom is, as more the V-O distance is lengthened. O(2), O(4) and O(7) atoms are bound to only one V atom, and are 1.59-1.65 Å distant from V. O(3) and O(6) atoms bridge two V atoms with the distances 1.77-1.96 Å. O(1) atom is shared by one Mn and 3.5 V atoms, of which lengths range from 2.08 to 2.38 Å. Five V-O(5) bond distances fall on between 2.28 and 2.38 Å. Therefore the coordinations around three independent V atoms are not the same.

One of the $3K^+$ ions, i.e.K(1), is tightly surrounded by 6 - 8 O atoms of the polyanions within the distance 2.8 Å. K(2) and K(3) have 5 and 3 coordination with average distances 2.8 and 2.9 Å, respectively. It is thought that there are some missing water molecules which may be zeolitic or disordered. The structure of $K_{10}[Mn_2V_{22}O_{64}].2H_2O$ and $K_5H_3[Mn_3V_{12}O_{40}].8H_2O$ will be published elsewhere.

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