Crystal structure of tetrapotassium dihydrogen heptatungsteno tetramolybdeno monomanganese monoaquasilicate hydrate, $K_4H_2[SiW_7Mo_4Mn(H_2O)O_{39}] \cdot 13H_2O$

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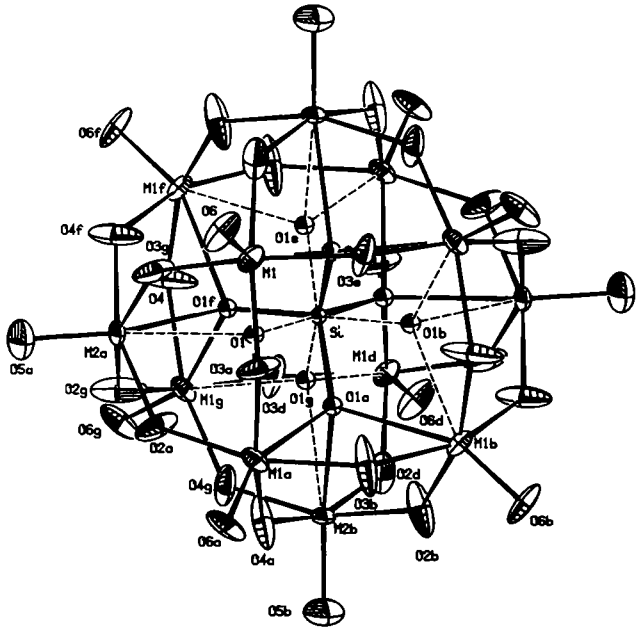

Abstract

$H_{30}K_4MnMo_4O_{53}SiW_7$, tetragonal, *P4/mnc* (No. 128), $a = 14.105(5)$ Å, $c = 12.476(7)$ Å, $V = 2482.1$ Å^3, $Z = 2$, $Rgt(F) = 0.064$, $wR_{ref}(F^2) = 0.154$, $T = 293$ K.

Source of material

$K_4H_2[SiW_7Mo_4Mn(H_2O)O_{39}] \cdot 13H_2O$ was synthesized by the method in situ degradation. $H_4SiW_8Mo_4O_{40} \cdot (20\text{-}25)H_2O$ (10 g), which was prepared according to the literature method [1], was dissolved in 100 ml of water at 353 K in the water-bath, $Mn(NO_3)_2$ (0.62 g) was added to this solution on stirring. The pH of the mixture solution was adjusted to pH = 4.7 – 5.0 with aqueous solution of KAc-HAc (KAc:HAc:H_2O = 15:3:30). The crystals of title compound was formed in a refrigerator at 270 K – 276 K. The components of the compound was determined by chemical analysis as follows. Manganese was estimated by DTPA methods (back-titration with standard zinc solution, in pH = 9.5 buffer in presence of Zn-agent). Molybdenum and tungsten in the compound was separated using literature methods [2], then Mo was weighed as MoO_3 after precipitation with α-benzoinoxime and tungsten was weighed as WO_3 after precipitation with cincholine. Potassium was weighed as $KB(C_6H_5)_4$ and silicon was estimated according to reference [3], the water content was estimated by TG. The presence of hydrogen atoms in the crystal structure was deduced in order to have charge balance, but their positions could not be determined. The content of manganese was determined by chemical analytical methods and it is supposed to be located at the same position as Mo and W because its content is very low.

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Discussion

The structure of $[SiW_7Mo_4Mn(H_2O)O_{39}]^{6-}$ is very similar to that of $[SiW_8Mo_4O_{40}]^{4-}$, which has the Keggin structure, but in the title compound, seven W, four Mo and one Mn atoms oriented randomly to one of the twelve positions and with the satistical weight of 7/12, 4/12 and 1/12, respectively. This compound is isostructural with $K_4H_2PMo_9V_3O_{40} \cdot 10H_2O$ [4]. The site symmetry of the molecule in the crystal is 4/*m*, which is incompatible with tetrahedral symmetry of the Keggin molecule. This apparent high symmetry is effected by orientational randomness of the anion $[SiW_7Mo_4Mn(H_2O)O_{39}]^{6-}$ in the crystal, and can be interpreted in the light of the model proposed by Sergienko and Pope [5-7]. The tetragonal structure contains normal Keggin anion disordered as whole in two position related by a 90° rotation about the anion 4 axis. For this reason, it seems that Si is surrounded by a cube of O atoms at 1.64(2) Å, with each O site half-occupied and M metal atoms (Mo, W, Ni) coordinated by seven O atoms. However, in an ordered model, the Si and M metal atoms are coordinated by four and six oxygen atoms, respectively, as shown in the figure. According to the number of atoms that the oxygen atom is coordinated to, there are three groups of the M—O bonds: (a) for M–O, the distances are 1.64(2) Å to 1.66(1) Å; (b) for M—O—M, 1.87(2) Å to 1.92(2) Å; (c) for Si—O—M3, 2.34(2) Å to 2.38(2) Å. The deformation of the Keggin anion $[SiMo_8W_4O_{40}]^{4-}$ caused by the replacement of one molybdenum atom by manganese could not be studied in detail because of its randomness. In addition, due to the 50% occupancy of O1 as well as the occupancy of three different atoms of different sizes at sites M1 and M2, the neighbouring oxygen atoms suffer disordering, which lead to the relative large and anisotropic displacement parameters of O2, O3, O5, Ow7, Ow8, and Ow10.

Table 1. Data collection and handling.

Crystal:	brown fragment, size 0.45 × 0.55 × 0.65 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	178.43 cm^{-1}
Diffractometer, scan mode:	Bruker SMART-CCD, φ
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9567, 1158
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1044
$N(param)_{refined}$:	91
Program:	SHELXTL [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
Si(1)	2*a*		0	0	0	0.012(2)
O(1)	16*i*	1/2	0.012(2)	0.095(2)	0.075(2)	0.017(5)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	16*i*	7/12	0.13823(7)	0.10921(8)	0.20000(8)	0.0275(6)	0.0348(6)	0.0262(6)	–0.0143(4)	–0.0045(4)	–0.0029(4)
Mo(1)	16*i*	4/12	0.13823	0.10921	0.20000	0.0275	0.0348	0.0262	–0.0143	–0.0045	–0.0029
Mn(1)	16*i*	1/12	0.13823	0.10921	0.20000	0.0275	0.0348	0.0262	–0.0143	–0.0045	–0.0029
W(2)	8*h*	7/12	0.24651(9)	–0.0281(1)	0	0.0120(7)	0.0289(8)	0.0421(9)	0.0031(6)	0	0
Mo(2)	8*h*	4/12	0.24651	–0.0281	0	0.0120	0.0289	0.0421	0.0031	0	0
Mn(2)	8*h*	1/12	0.24651	–0.0281	0	0.0120	0.0289	0.0421	0.0031	0	0
K(1)	8*h*		0.2967(5)	0.2447(5)	0	0.047(4)	0.053(4)	0.033(3)	–0.028(4)	0	0
O(2)	16*i*		0.235(2)	0.069(1)	0.105(2)	0.13(2)	0.028(8)	0.07(1)	0.001(9)	0.08(1)	–0.006(8)
O(3)	16*i*		0.129(2)	–0.016(1)	0.255(2)	0.14(2)	0.020(8)	0.11(2)	–0.02(1)	0.10(2)	–0.016(9)
O(4)	16*i*		0.122(1)	0.212(2)	0.105(2)	0.020(7)	0.12(2)	0.08(1)	0.010(9)	0.009(8)	0.07(1)
O(5)	8*h*		0.365(2)	–0.044(2)	0	0.03(1)	0.08(2)	0.09(2)	0.01(1)	0	0
O(6)	16*i*		0.203(1)	0.158(1)	0.296(1)	0.06(1)	0.07(1)	0.031(8)	–0.046(9)	–0.005(7)	–0.016(8)
Ow(7)	8*h*		0.319(3)	0.442(2)	0	0.14(3)	0.08(2)	0.11(3)	0.01(2)	0	0
Ow(8)	8*g*		0.407(1)	–*x* + 1/2	1/4	0.035(7)	U11	0.16(3)	0.01(1)	–0.03(1)	U13
Ow(9)	4*e*	1/2	1/2	1/2	0.065(4)	0.07(3)	U11	0.01(3)	0	0	0
Ow(10)	8*g*		0.113(2)	–*x* + 1/2	1/4	0.14(2)	U11	0.14(3)	0.06(3)	–0.08(2)	U13

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