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Synthesis and Structure of Transition-Metal-Containing Tungstomolybdosilic Polyoxometalates and their Catalytic Performance in Oxidation of Cyclohexene with Hydrogen Peroxide

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SYNTHESIS AND STRUCTURE OF TRANSITION-METAL-CONTAINING TUNGSTOMOLYBDSILIC POLYOXOMETALATES AND THEIR CATALYTIC PERFORMANCE IN OXIDATION OF CYCLOHEXENE WITH HYDROGEN PEROXIDE

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A series of title complexes with the general molecular formula, $K_4H_2[SiW_7Mo_4Me(H_2O)_{39}] \cdot xH_2O$ (denoted as MeW_7 ; $Me = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$), were synthesized. IR spectra, electronic spectra, XPS spectra and thermal analyses were systematically recorded. The crystal structure of MnW_7 , determined from single-crystal X-ray diffraction at 293 K, belongs to the tetragonal system, space group $P4/mnc$, $Z = 2$, $a = 1.4105(5)$ and $c = 1.2476(7)$ nm. These samples were investigated for the oxidation of cyclohexene with H_2O_2 , and showed more activity than their corresponding parent compounds.

Keywords: Polyoxometalate; Tungstomolybdsilicate; Transition element; Catalytic oxidation; Cyclohexene

INTRODUCTION

Polyoxometalates constitute a large category of compounds having high potential for theoretical contributions and for practical applications [1–4]. These species are remarkable for their molecular and electronic structural diversity and their significance in quite diverse disciplines, e.g. catalysis, medicine and materials science [5–8]. Studies indicate that lacunary polyoxometalate anions as ligands coordinated with transition metal ions can be considered inorganic analogues of metalloporphyrins [9]. Considered to be the most robust homogeneous oxidation catalysts at the present time, they show remarkable stability, activity, selectivity and resistance to oxidative degradation under catalytic reaction conditions. Although there have been many reports of lacunary polyoxometalate ligands containing one kind of addendum atom, lacunary species with two or more elements as addendum atoms are rarely observed [10].

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In the work reported in this article, we synthesized a series of new tetrabasic tungstomolybdsilic complexes with transition elements and simultaneously investigated their structure, properties and catalytic activity in the oxidation of cyclohexene. These complexes offer new experimental materials to elucidate the correlation of catalytic activity and structures of the polyoxometalates in a systematic way. The structural specificity for the substrates and mechanism of catalysis can also be studied.

EXPERIMENTAL

Synthesis Method

Tungstomolybdsilic acid crystals $\text{H}_4\text{SiMo}_4\text{W}_8\text{O}_{40} \cdot (20\text{--}25\text{H}_2\text{O})$ (10 g), synthesized by the acidification etherate method according to the literature [11], were dissolved in water (100 cm^3) and heated to 353 K in a beaker. The corresponding transition metal nitrate was then added with stirring. The pH of the solution was adjusted to 4.7–5.0 with a buffered aqueous solution of KAc–HAc (KAc:HAc:H₂O = 15:3:30). The reaction mixture was stirred for 30 min at 353 K, and then filtered. Crystals of the title compounds were formed in a refrigerator at 273–276 K.

Component Analysis and Characterization

Transition elements were estimated by DTPA titration (back-titration with standard zinc solution, in pH 9.5 buffer in presence of Zn agent). Molybdenum and tungsten in the same compound were separated by the method described elsewhere [12], then molybdenum was weighed as MoO_3 after precipitation with α -benzoinoxime and tungsten was weighed as WO_3 after precipitation. Potassium was weighed as $\text{KB}(\text{C}_6\text{H}_5)_4$ and silicon was estimated according to reference [13]; the water content was estimated by thermogravimetric analysis (TGA). IR, electronic, XPS spectra and thermal analysis were recorded, respectively, on the instruments listed below: NEXUS 670 FT-IR spectrophotometer (Nicolet, USA); 265 UV spectrophotometer (Shimadzu, Japan); PHI-5100 X-ray photoelectron spectrometer (P.E., USA), using an Al/Mg bianode, resolving power 0.8 eV (Ag 3d_{5/2}), target power 390 W, sensitivity 40 K, binding energies are referred to the C (1 s) line 285.6 eV; TG-SDTA 851 e (Mettler, Switzerland); D8 ADVANCE X-ray powder diffractometer (Bruker, Germany), Cu target K $\alpha\lambda = 1.5418\text{ \AA}$.

X-ray Data Collection and Structure Determination

The data for $\text{MnW}_7(0.35 \times 0.25 \times 0.20\text{ mm}^3)$ were collected at 293(2) K on a Bruker SMART-CCD diffractometer (Bruker, Germany) using a Mo anode and graphite monochromator ($\lambda = 0.071073\text{ nm}$). Intensity data with 2θ values in the range 4–54.1° were collected using ω scans. A total of 1158 reflections with $I \geq 2\sigma(I)$ among 2855 unique reflections collected were used for structure determination. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on F^2 using the SHELXTL program [14]. All hydrogen atoms other than those of some water molecules were directly located from the difference Fourier map and included in the structure, but not refined.

Catalytic Performance in Oxidation of Cyclohexene

The catalytic oxidation of cyclohexene with H_2O_2 using the different catalysts was carried out in a two-neck glass vessel (50 cm^3) jacketed for circulation of water and fitted with a condenser. Cyclohexene (9.8 mmol), CHCl_3 (10 cm^3) and catalyst (0.073 mmol) were added to the reactor and the reaction mixture was heated to 283 K with magnetic stirring. Then 30% H_2O_2 (8 mmol) was added as oxidant. The products were analyzed on an Agilent HP 6850 Series gas chromatograph equipped with a IFP detector and HP-1 column ($L = 30\text{ m}$; $\Phi = 0.32\text{ mm}$) after 4-h reaction.

RESULTS AND DISCUSSION

Synthesis and Composition Analysis

Two principal synthetic methods for polyoxometalates with transition metals have been reported [15,16]. One is reaction of lacunary polyoxometalate anions and transition metal ions, the other is by *in situ* reaction of salts containing the components. In general, the first method was adopted for stable lacunary polyoxometalate anions. The $[\text{SiMo}_4\text{W}_7\text{O}_{39}]^{8-}$ anion has not been reported in the literature. Our work has demonstrated that $[\text{SiMo}_{12-n}\text{W}_n\text{O}_{40}]^{4-}$ would degrade and produce the lacunary anion $[\text{SiMo}_{11-n}\text{W}_n]^{8-}$ under suitable conditions [17], but is not stable enough to be separated. In the presence of transition metal ions in solution, as soon as the lacunary anions form, they coordinate with transition metals leading to stable polyoxometalates with transition metal elements.

The new compounds possess a fine crystal-like appearance and are easily effloresce but do not decompose when exposed to air for a long time. The results of analysis shown in Table I indicate that the general anionic formula is $[\text{SiW}_7\text{Mo}_4\text{Me}(\text{H}_2\text{O})\text{O}_{39}]^{6-}$ ($\text{Me} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+}).

IR Spectra

Table II shows the vibration frequencies of the title compounds between 700 and 1000 cm^{-1} , with those of the related compound KSiMo_4W_8 for comparison. Both these polyoxometalates contain the basic characteristics of Keggin structures during the degradation and coordination with transition metal ions. Since the tungsten atom is substituted by a transition element atom carrying lower charge, there is a decrease

TABLE I Results of component analysis for the complexes synthesized

Complex	Content (%) ^a					
	Me	Si	Mo	W	H ₂ O	K
MnW ₇ ·24H ₂ O	1.85 (1.84)	0.94 (0.94)	12.84 (12.85)	43.08 (43.10)	15.07 (15.07)	5.23 (5.24)
CoW ₇ ·23H ₂ O	1.98 (1.98)	0.95 (0.93)	12.92 (12.91)	43.32 (43.31)	14.52 (14.33)	5.27 (5.26)
NiW ₇ ·25H ₂ O	1.93 (1.95)	0.94 (0.93)	12.76 (12.76)	42.80 (42.79)	15.56 (15.56)	5.19 (5.20)
CuW ₇ ·22H ₂ O	2.14 (2.15)	0.95 (0.95)	12.98 (12.97)	43.52 (43.50)	13.97 (13.99)	5.23 (5.26)
ZnW ₇ ·23H ₂ O	2.17 (2.19)	0.94 (0.94)	12.88 (12.88)	43.24 (43.21)	14.52 (14.50)	5.23 (5.25)
CdW ₇ ·22H ₂ O	3.73 (3.74)	0.93 (0.93)	12.74 (12.76)	42.82 (42.80)	13.78 (13.76)	5.16 (5.20)

^aTheoretical values in parentheses.

TABLE II IR spectral data of the complexes (cm⁻¹)

Complex	Band assignment					
	$\nu_{as}M-Od$	$\nu_{as}Si-Oa$	$\nu_{as}M-Ob-M$	$\nu_{as}M-Oc-M$	ν_8Si-Oa	
KS ₂ Mo ₄ W ₈	975	921	876		790	538
MnW ₇	951	896		801 745	696	534
CoW ₇	951	898		797 732	698	533
NiW ₇	955	901		807	697	537
CuW ₇	954	898		792 734	686	520
ZnW ₇	953	898		800 748	697	537
CdW ₇	946	886		796	722	535

in the asymmetric stretching frequency of M–Od of the anion in contrast to that of KS₂Mo₄W₈. The asymmetric stretching frequency of the Si–Oa bond also decreases, owing to the reduction of the force constant of the corresponding bond. The $\nu_{as}M-Ob-M$ (M = Mo, W, Me) bands disappeared while $\nu_{as}M-Oc-M$ bands are split into two or three bands in the IR spectra, in agreement with the results of molybdosilicate complexes containing rare earth elements [17]. It is reasonable to attribute this to the different degree of distortion between the six-member ring M–Oc–M–Oc–M–Oc in one M₃O₁₃ and the six-member ring M–Ob–M–Oc–M–Ob between different groups in the molecule structure, resulting in the decrease of vibration intensity. As a result, the primary weak $\nu_{as}M-Ob-M$ bands of the Keggin structure in KS₂Mo₄W₈ become weak enough to be covered by $\nu_{as}Si-O$, while the stronger bands of $\nu_{as}M-Oc-M$ split. As depicted in Table II, the split of the $\nu_{as}M-Oc-M$ band is different for different transition element compounds. For example, the $\nu_{as}M-Oc-M$ band in IR spectra of the compounds NiW₇ and CdW₇ splits into two, but others show three bands; the minimum value of the split is 74 cm⁻¹ and the maximum is 110 cm⁻¹. Evidently the ion radius, electron number and outer shell electronic structure of transition element affect the structure and characteristics of bonds of multicomponent polyoxometalates with transition metals.

Electronic Spectra

The electronic spectra are composed of two parts; the spectra of ligands in the ultraviolet region and transition element ions in the visible region (see Table III). The charge-transfer bands, including charge transfer from terminal oxygen atom (Od) to molybdenum or tungsten (i.e., M → Od) and that from the bridging oxygen atom to Mo or W (i.e., M → Ob,c) are in the range 200–450 nm. We can conclude from Table III that different transition metal ions have little effect on the electronic structure of the polyoxometalate ligands, and the M → Ob,c charge-transfer bands cannot be observed due to lengthened O–M bonds. This agrees with the red shift of the corresponding band in IR spectra of the new compounds. From theoretical considerations [18], there are three absorption bands for Co²⁺(3d⁷) and Ni²⁺(3d⁸) caused by d–d transitions: ${}^4T_{1g}({}^4F) \rightarrow {}^4F_{2g}({}^4F)$, ${}^4T_{1g}({}^4F) \rightarrow {}^4A_{2g}({}^4F)$, ${}^4F_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4P)$ and ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{2g}({}^3F)$, ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3F)$, ${}^3A_{2g}({}^3F) \rightarrow {}^3T_{1g}({}^3F)$, while Cu²⁺(d⁹) has only one absorption band corresponding to the transition of ${}^2E_g({}^2D) \rightarrow {}^2T_{2g}({}^2D)$. As shown in Table III, it is obvious that some absorption bands of the d–d transition

TABLE III Electronic spectral data of the complexes (nm)

Assignment	$M \rightarrow Od$	$M \rightarrow Ob,c$	$d \rightarrow d$ transition
KSiMo ₄ W ₈	219.6	280.0	
MnW ₇	218.0		
CoW ₇	219.8		554.0
NiW ₇	218.0		697.8 80.0–800.0
CuW ₇	218.0		865.2
ZnW ₇	219.6		
CdW ₇	221.0		
[Co(H ₂ O) ₆] ²⁺			510.7
[Ni(H ₂ O) ₆] ²⁺			655.8 720.4
[Cu(H ₂ O) ₆] ²⁺			788.8

TABLE IV Binding energies of electron in the inner shell of constituent elements for the new complexes and their oxides

Complex	Si $2p_{3/2}$	W $4f_{7/2}$	Mo $3d_{5/2}$	O $1s$	M $2p_{3/2}$	M $2p_{1/2}$
NiW ₇	101.83	35.33	232.56	530.15	855.77	873.78
ZnW ₇	101.51	35.46	232.56	530.24	1021.67	1044.45
CuW ₇	102.15	36.15	233.69	531.28	935.15	954.86
ZnO					1021.70	1044.70
NiO					853.30	871.70
KSiMo ₄ W ₈	102.73	36.52	233.71	531.82		

are covered by the strong absorption attributable to the ligands in the range 200–450 nm. CoW₇ has only one absorption band at 554.0 nm red shifted 43.3 nm in comparison to its aquo ions. A strong absorption band can be observed at about 865 nm for the CuW₇ complex red shifted about 76.4 nm. The UV spectra of NiW₇ show more differences from Ni²⁺ aquo ions. Not only does a red shift appear, but also its width and intensity change. For Ni²⁺ complexes, the two distinguishable bands between 650 nm and 720 nm in aquo ions become a single wider, asymmetric band with double structure; moreover its intensity decreases significantly in NiW₇. The coordination ability of polyoxometalate ligands is stronger than that of water. It is also seen that stronger delocalization of d-orbital electrons weakens the repulsion among themselves, which shortens the distance among the multiple terms.

XPS Spectra

Table IV exhibits the binding energies of electrons in the inner shell of the component elements for some of the compounds. In comparison to potassium tungstomolybdosilicate, the binding energies of electrons become lower. The new compounds illustrate that when transition metal ions with smaller radius replace Mo⁶⁺, the decreased positive charge spreads evenly over each element through inner O atom (Oa) and outer O atoms (Ob, Oc) of each ligand hole. For lanthanides with larger radius, it can spread only over through the four outer oxygens [17]. These results further confirm that transition element ions bind Oa of the polyoxometalate ligand.

The binding energies of inner-shell electrons of the transition elements in polyoxometalate complexes are higher than in their oxides, e.g., in NiO, the binding energies of electrons in 2P_{3/2} and 2P_{1/2} of Ni are 853.30 eV and 871.70 eV, respectively, but

they become 855.77 eV and 873.78 eV in the new complex (NiW_7). The increase in binding energies demonstrates that the electron density around the transition element decreases and part of the negative charge on the transition metal moves to polyoxometalate ligands. Meanwhile, the change of binding energies from transition metals with fully, occupied d-electronic shells is smaller, e.g., for $\text{Zn}^{2+}(\text{d}^{10})$, the binding energies of electron in the inner shell of $2\text{P}_{3/2}$ and $2\text{P}_{1/2}$ of ZnO are 1021.70 eV and 1044.70 eV, respectively, and are 1021.67 eV and 1044.45 eV in ZnW_7 . These results, together with the red shift and splitting of IR bands, fully demonstrate that the d-electronic structure in the outer shell of transition element ions has an important effect on the electronic structure of complexes between transition elements and polyoxometalate ligands. When the d-electron orbital is not fully occupied, d-electron content in this chemical bond increases and the delocalization of d-electrons is stronger. The attractive ability of the polyoxometalate ligand for electrons is much stronger than that of O^{2-} ions.

Thermal Decomposition of the Compounds

The thermal behavior of the compounds was studied by thermogravimetric (TG), differential thermal analysis (DTA), IR spectroscopy and X-ray powder diffraction at different temperatures. The TG and DTA curves of all new compounds are very similar, indicating that their decomposition processes are similar and transition elements have little effect.

The TG curve for CoW_7 shows a gradual loss of weight starting from 27°C and continuing up to 384°C , in three stages: the first (I) is around $26.8\text{--}100.3^\circ\text{C}$; second (II), $100.3\text{--}165.7^\circ\text{C}$; and third (III), $165.7\text{--}384.4^\circ\text{C}$ (See Fig. 1). In stages I and II the weight loss is rapid, and two endothermic peaks are observed on DTA curves at 69.8°C and 125.4°C . As shown in Figs. 2 and 3, the IR spectra do not change, but a number of X-ray powder diffraction peaks of the complex diminish above 80°C , and there are only two diffraction peaks at 300°C ($2\theta: 10, 18$). In the first two steps, the weight loss is due to elimination of zeolite and crystal water, accompanying the powdering of crystal, but the complex molecules are not destroyed. In the third region, the

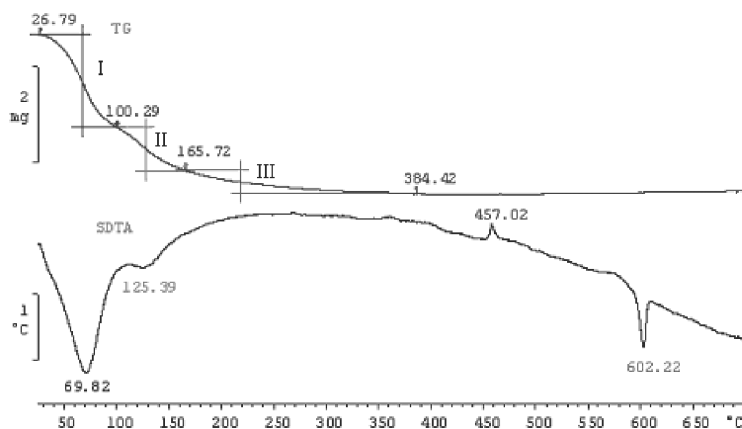


FIGURE 1 Thermal analysis curve of CoW_7 .

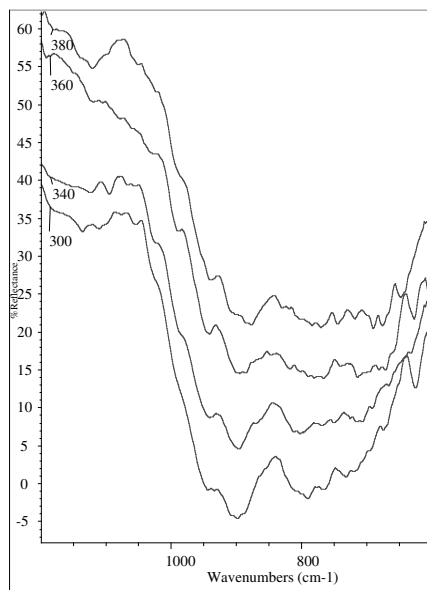


FIGURE 2 IR spectra of CoW_7 at four different temperatures (300°C; 340°C; 360°C; 380°C).

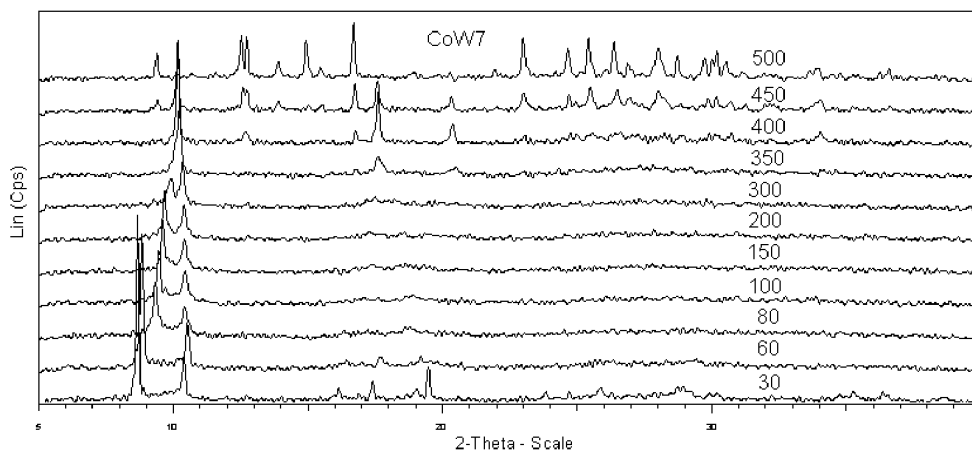


FIGURE 3 Powder XRD pattern of CoW_7 .

weight loss is mainly structural water. There is an exothermic peak (457.0°C) on the differential thermal curve. The IR spectra of the sample at 340°C and 360°C are obviously different, indicating that the Keggin structure remains at 340°C, but not at 360°C. The X-ray powder diffraction patterns of the sample at 340°C and 400°C are also different, the latter having more diffraction peaks than the former, showing that decomposition is accompanied by loss of structural water. The decomposition temperature is between 340°C and 380°C. The exothermal peak at 457.0°C on DTA curves is caused by the crystallization of a part of the decomposed product. Further heating shows no change in the TG curve. One stronger endothermic peak at 602.2°C is observed, due to melting of the decomposed products.

Crystal Structure

Crystallographic data are listed in Tables V–VII. The structure, built up from $[\text{SiW}_7\text{Mo}_4\text{Mn}(\text{H}_2\text{O})\text{O}_{39}]^{6-}$ anions, K^+ ions and H_2O molecules, is isostructural in space group $P4/mnc$ with $\text{K}_4\text{H}_2\text{PMo}_9\text{V}_3\text{O}_{40} \cdot 10\text{H}_2\text{O}$ [19] and $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_4 \cdot 30\text{H}_2\text{O}$ [20]. The site symmetry of the molecule in the crystal is $4/m$, which is incompatible with the tetrahedral symmetry of the Keggin molecule. The central SiO_4 group must be disordered, as indicated by the fact that Si is surrounded by a cube of O atoms at 1.69 Å, with each O site half-occupied to satisfy the needs of the $4/m$ symmetry (see Fig. 4), so that M metal ions (Mo, W, Mn) coordinate seven O atoms and Si ion coordinates eight O atoms (Fig. 4). The result is that these tetrahedral structures contain normal Keggin molecules disordered as a whole in two positions related by a 90° rotation about the molecular four-fold axis. This model was originally proposed for these crystal structures by Sergienko *et al.* [21] and was later confirmed by Evans and Pope [22].

The $[\text{SiW}_7\text{Mo}_4\text{Mn}(\text{H}_2\text{O})\text{O}_{39}]^{6-}$ group has a Keggin structure and consists of a central SiO_4 tetrahedron surrounded by twelve MO_6 octahedra. The twelve octahedra may be subdivided into four M_3O_{13} groups. In these groups each MO_6 octahedron is linked to its neighbor on either side by a shared edge making one corner common to the three octahedra. The four groups are then linked to each other by sharing corners and to the SiO_4 tetrahedron by three-coordinate oxygen atoms. This Keggin anion lies in

TABLE V The experimental conditions and crystallographic data for $\text{K}_4\text{H}_2[\text{SiW}_7\text{Mo}_4\text{Mn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 24\text{H}_2\text{O}$

Empirical formula	$\text{K}_4\text{H}_2[\text{SiW}_7\text{Mo}_4\text{Mn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 24\text{H}_2\text{O}$
Space group	$P4/mnc$
a (nm)	1.4105(5)
b (nm)	1.4105(5)
c (nm)	1.2476(7)
V (nm ³)	2.4823(19)
Calculated density (D_c) (g cm ⁻³)	3.904
Z	2
T (K)	293(2)
Absorption coefficient (μ) (mm ⁻¹)	18.762
$\lambda(\text{Mo K}\alpha)$ (nm)	0.071073
No. independent reflections	2855
No. observations	1158($I > 2s(I)$)
Final R^a	0.0668
wR^b	0.1620
Goodness of fit on F^2	1.215

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

TABLE VI Selected bond lengths (0.1 nm) for $\text{K}_4\text{H}_2[\text{SiW}_7\text{Mo}_4\text{Mn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 13\text{H}_2\text{O}$

M1–O6	1.649(13)	M2–O5	1.66(3)	Si–O1#3	1.69(2)
M1–O3#1	1.871(17)	M2–O2#3	1.902(18)	Si–O1#2	1.69(2)
M1–O4	1.898(18)	M2–O2	1.902(18)	Si–O1	1.69(2)
M1–O2	1.899(17)	M2–O4#4	1.923(17)	Si–O1#4	1.69(2)
M1–O3	1.904(17)	M2–O4#2	1.923(17)	Si–O1#5	1.69(2)
M1–O1	2.35(2)	M2–O1#4	2.33(2)	Si–O1#6	1.69(2)
M1–O1#2	2.36(2)	M2–O1#2	2.33(2)	Si–O1#1	1.69(2)
				Si–O1#7	1.69(2)

$$M = 7/12 \text{ W} + 4/12 \text{ Mo} + 1/12 \text{ Mn}.$$

TABLE VII Selected bond angles ($^{\circ}$) for $K_4H_2[SiW_7Mo_4Mn(H_2O)O_{39}] \cdot 13H_2O$

O6-M1-O3#1	100.5(11)	O5-M2-O2#3	100.8(11)	O1#3-Si1-O1#2	109.4(8)
O6-M1-O4	101.4(10)	O5-M2-O2	100.8(11)	O1#3-Si1-O1	70.3(15)
O3#1-M1-O4	90.1(7)	O2#3-M2-O2	87.1(12)	O1#2-Si1-O1	70.6(8)
O6-M1-O2	99.8(10)	O5-M2-O4#4	98.2(10)	O1#3-Si1-O1#4	70.6(8)
O3#1-M1-O2	159.7(12)	O2#3-M2-O4#4	90.7(7)	O1#2-Si1-O1#4	70.3(15)
O4-M1-O2	85.5(8)	O2-M2-O4#4	161.0(10)	O1-Si1-O1#4	109.4(8)
O6-M1-O3	99.3(11)	O5-M2-O4#2	98.2(10)	O1#3-Si1-O1#5	109.7(15)
O3#1-M1-O3	87.7(12)	O2#3-M2-O4#2	161.0(10)	O1#2-Si1-O1#5	109.4(8)
O4-M1-O3	159.7(11)	O2-M2-O4#2	90.7(7)	O1-Si1-O1#5	180.0(17)
O2-M1-O3	89.4(7)	O4#4-M2-O4#2	85.3(12)	O1#4-Si1-O1#5	70.6(8)
O6-M1-O1	156.7(9)	O5-M2-O1#4	155.3(6)	O1#3-Si1-O1#6	70.6(8)
O3#1-M1-O1	63.5(8)	O2#3-M2-O1#4	64.5(9)	O1#2-Si1-O1#6	180.0(17)
O4-M1-O1	63.9(10)	O2-M2-O1#4	98.2(10)	O1-Si1-O1#6	109.4(8)
O2-M1-O1	97.0(10)	O4#4-M2-O1#4	64.0(9)	O1#4-Si1-O1#6	109.7(15)
O3-M1-O1	96.9(10)	O4#2-M2-O1#4	97.2(10)	O1#5-Si1-O1#6	70.6(8)
O6-M1-O1#2	154.3(9)	O5-M2-O1#2	155.3(6)	O1#3-Si1-O1#1	109.4(8)
O3#1-M1-O1#2	97.2(10)	O2#3-M2-O1#2	98.2(10)	O1#2-Si1-O1#1	109.7(15)
O4-M1-O1#2	97.1(10)	O2-M2-O1#2	64.5(9)	O1-Si1-O1#1	70.6(8)
O2-M1-O1#2	63.9(9)	O4#4-M2-O1#2	97.2(10)	O1#4-Si1-O1#1	180.0(17)
O3-M1-O1#2	62.8(9)	O4#2-M2-O1#2	64.0(9)	O1#5-Si1-O1#1	109.4(8)
O1-M1-O1#2	48.9(10)	O1#4-M2-O1#2	49.2(12)	O1#6-Si1-O1#1	70.3(15)
O1#3-Si1-O1#7	180.0(17)	O1#2-Si1-O1#7	70.6(8)	O1-Si1-O1#7	109.7(15)
O1#4-Si1-O1#7	109.4(8)	O1#5-Si1-O1#7	70.3(15)	O1#6-Si1-O1#7	109.4(8)
O1#1-Si1-O1#7	70.6(8)				

M = 7/12 W + 4/12 Mo + 1/12 Mn.

Symmetry transformations used to generate equivalent atoms:

#1: $-y, x, z$; #2: $y, -x, z$; #3: $x, y, -z$; #4: $y, -x, -z$; #5: $-x, -y, -z$; #6: $-y, x, -z$; #7: $-x, -y, z$; #8: $-y + 1/2, -x + 1/2, -z + 1/2$; #9: $-y + 1/2, -x + 1/2, z - 1/2$; #10: $-y + 1/2, -x + 1/2, z + 1/2$; #11: $-x + 1, -y + 1, -z$.

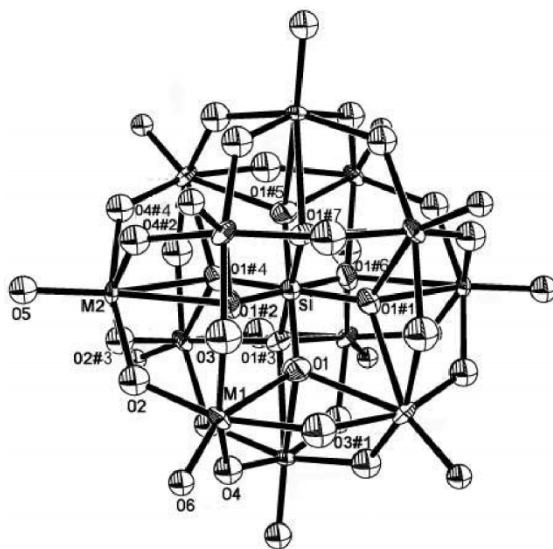


FIGURE 4 Crystal structure of anion $[SiMo_4MnW_7(H_2O)O_{39}]^{6-}$, showing atom numbering scheme. $M = 1/12 Mn + 4/12 Mo + 7/12 W$.

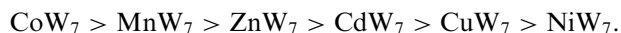
the crystal with its seven W, four Mo and one Mn sites oriented randomly to one of the twelve positions and with the statistical weight of 7/12, 4/12 and 1/12, respectively. The deformation of the Keggin structure anion $[SiMo_4W_8O_{40}]^{4-}$ caused by the replacement of one tungsten atom could not be studied in detail because of this randomness.

TABLE VIII The conversion of substrates and the selectivity of products in the oxidation of cyclohexene

Catalyst	Product conversion (%)			Selectivity (%)			Cyclo-hexene conversion (%)
	Cyclo-hexenone	Cyclo-hexenol	Cyclo-hexene oxides	Cyclo-hexenone	Cyclo-hexenol	Cyclo-hexene oxides	
CoW ₇	12.1	5.0	6.0	52.3	21.6	26.0	23.1
NiW ₇	1.6	0	1.6	50.0	0	50.0	3.2
CuW ₇	0.5	4.0	0	11.1	88.9	0	4.5
MnW ₇	12.0	6.0	3.0	57.1	28.5	14.3	21.0
ZnW ₇	5.0	0	2.7	64.9	0	35.1	7.7
CdW ₇	3.0	0	1.99	61.2	0	38.8	4.9
KSrMo ₄ W ₈	0	0	0	0	0	0	0

Oxidation of Cyclohexene with H₂O₂ Catalyzed by MeW₇

When cyclohexene is introduced into MeW₇/H₂O₂ solution, the products of oxidation are cyclohexenone, cyclohexenol and cyclohexene oxides. The conversion of substrates and the selectivity of products in the oxidation of cyclohexene are summarized in Table VIII. By comparing with the inactivity of precursors, the corresponding tetrabasic polyoxometalates give irregular catalytic activity displayed as below:



It can be hypothesized that the improvement of catalytic activity is due to the introduction of transition metallic ions.

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