Electronic Supplementary Information

Two Novel Trivacant Keggin-type Polyoxometalates Supported Manganese Carbonyl Derivatives Synthesized by Degradation of Metastable $[\gamma\text{-}XW_{10}O_{36}]^{8-}$ (X = Ge^{IV}, Si^{IV})

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1. The bond valence sum calculations.

Considering the charge balance of **1** and **2**, some protons need to be added. Based on the considerations of that the polyoxotungstate fragments $[(OC)_3Mn(A\text{-}\alpha\text{-}H_2XW_9O_{34})]^{8-}$ (X = Ge, Si) polyoxoanions in the products have high negative charges and rich surface oxygen atoms, bond valence sum calculations of the oxygen atoms on POMs fragments (except O_{16}, O_{17}, O_{20}) are carried out (Table S1 and S2) to locate the positions of two protons in **1** and **2**, respectively. For **1**, there are twenty O atoms with their Σs in the range of –2.14~–1.90, eleven O atoms with their Σs in the range of –1.88~–1.60. As for **2**, there are thirteen O atoms with their Σs in the range of –2.13~–1.90, twelve O atoms with their Σs in the range of –1.89~–1.70 and six in the range of –1.67~–1.54. Therefore, it is likely that two protons are assigned to be delocalized on the whole polyoxoanion for charge balance. Some documents have confirmed that the considerable amounts of the protons may merge in the POMs for balancing the negative charges. Herein, some representative examples are given, such as $[(H_3O)_9\{(PY_2W_{10}O_{38})_4(W_3O_{14})\}]^{21-}$ and $[(H_3O)_{13.5}\{(PEu_2W_{10}O_{38})_4(W_3O_{14})\}]$,[1] $[H_{12}V_{13}O_{40}]^{3-}$,[2] $[\varepsilon\text{-}H_4PMo^{V}{}_8Mo^{VI}{}_{36}O_{40}\{La(H_2O)_4\}_4]^{5+}$,[3] $[Ni_{20}P_4W_{34}(OH)_4O_{136}(enMe)_8(H_2O)_6]^{12-}$,[4] $[H_{56}P_8W_{48}Fe_{28}O_{248}]^{28-}$ and $[H_{55}P_8W_{49}Fe_{27}O_{248}]^{28-}$.[5]

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2. The magnetic studies on compound 1.

The magnetic susceptibility of compound **1** was measured in the 2.7-300 K temperature range under a 2 KOe applied field and is shown as χ_m and χ_mT versus T plots in Figures S5. The χ_m value has not significant change upon increasing of the temperature form 2.7 K to 300 K. The χ_mT value gradually increases upon increasing of the temperature to reach a maximum (0.20 emu K mol^{-1} at 300 K), which is sharply lower than the expected value 3.00 emu K mol^{-1} (g = 2.0) of isolated high-spin Mn^{+} ion (s = 2). Therefore, the spin state of Mn ion is low-spin. The result is good agreement with the XPS analysis.

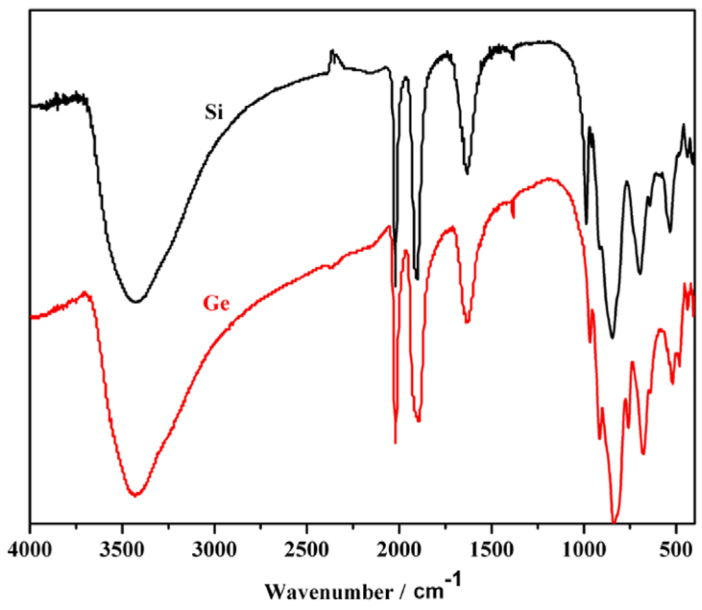

Fig. S1 IR spectra of **1** and **2.**

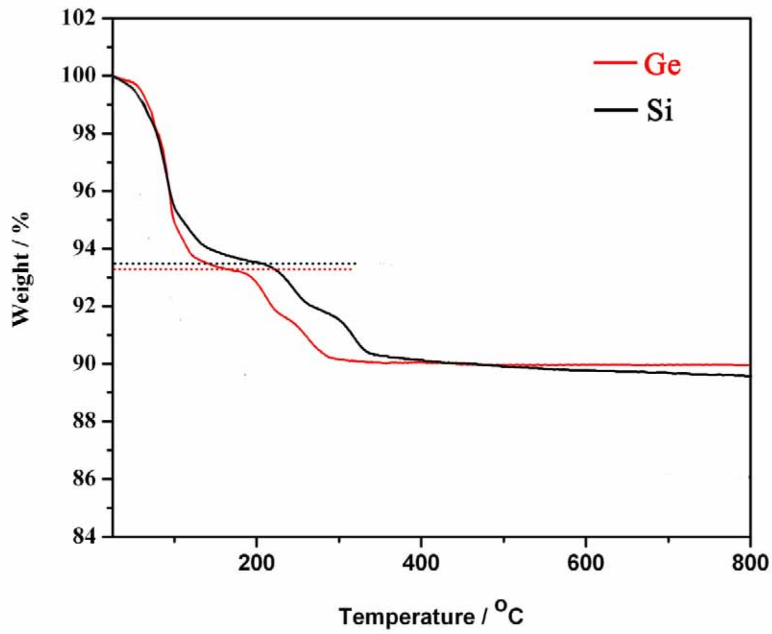

Fig. S2 The TG curves of **1** and **2**.

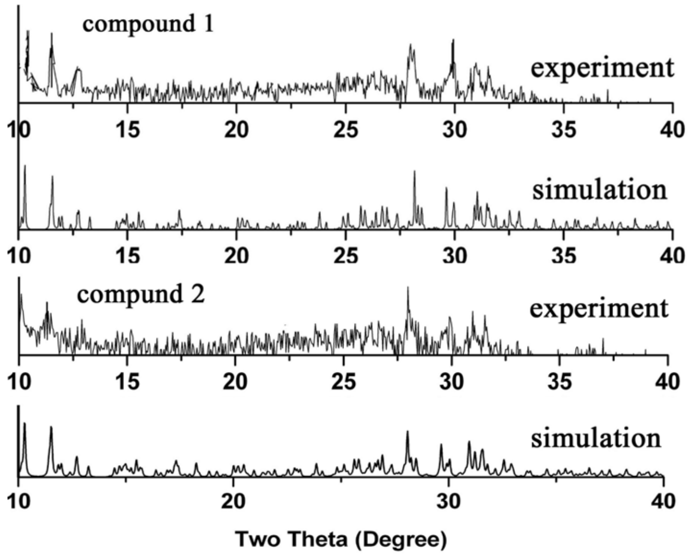

Fig. S3 Comparison of the simulated and experimental XRPD patterns: **1** a) and **2** b)

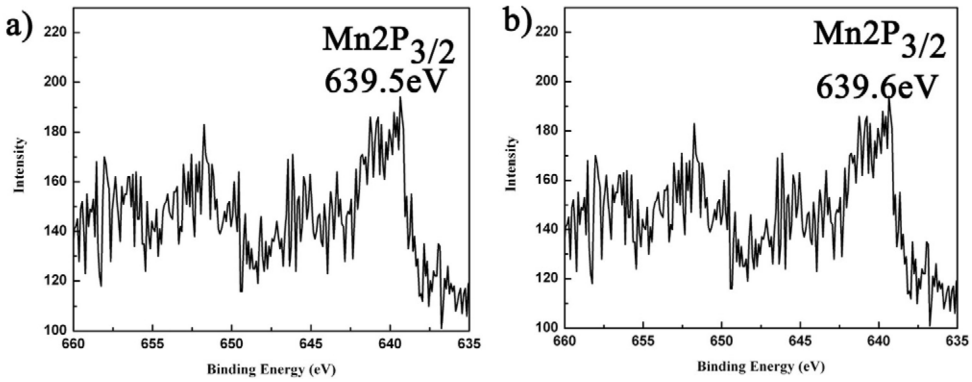

Fig. S4 The XPS spectra of **1** and $Mn(CO)_5Br$.

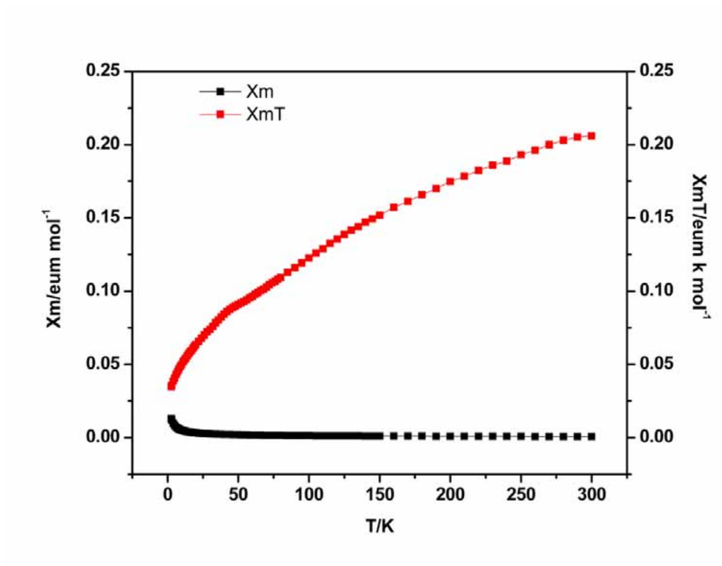

Fig. S5 The plots of χ_mT and χ_m as a function of T for **1**. The data were recorded in an applied field of 2 kOe.

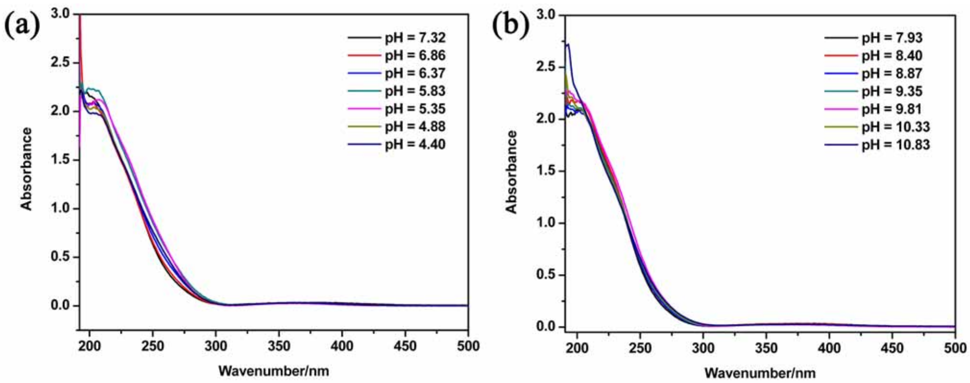

Fig. S6. Uv spectra of **1**. The stable pH range is about 5.8–9.8

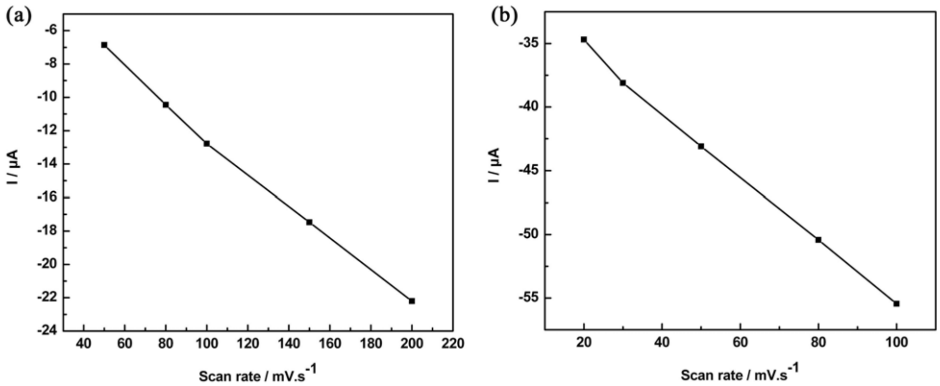

Fig. S7 (a) The variation of the CV cathodic peak currents with increasing scan rates from 50 to 200 mVs^{-1} of **1**. (b) The variation of the CV cathodic peak currents with increasing scan rates from 20 to 100 mVs^{-1} of **2**. A 3 mm diameter glassy carbon disk electrode (GCE) was used as a working electrode, a platinum wire served as the counter electrode and an Ag/AgCl electrode as the reference electrode

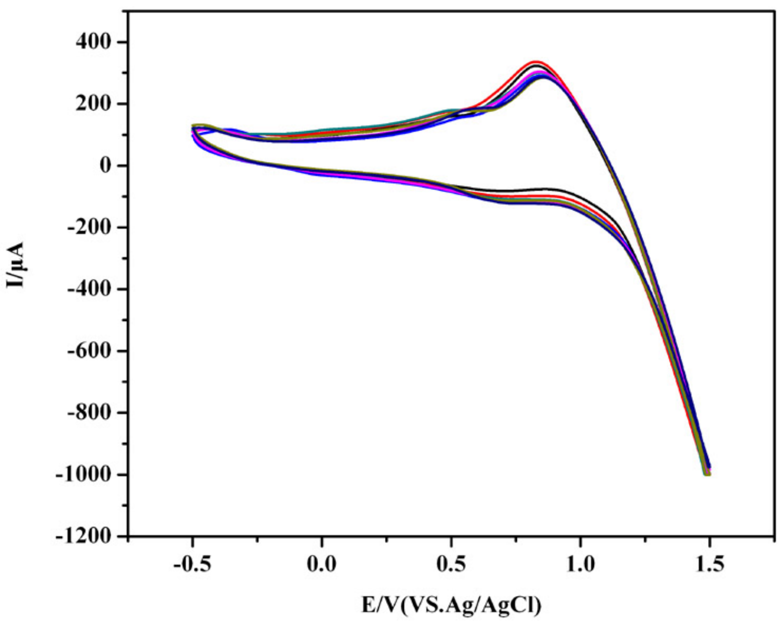

Fig. S8 Cyclic voltammograms of $Mn(CO)_5Br$ with different concentrations of $NaNO_2$: 0, 0.5, 1.5, 2.5, 3.5, 4.5, and 5.0 mM, respectively at scan rate of $100mVs^{-1}$.

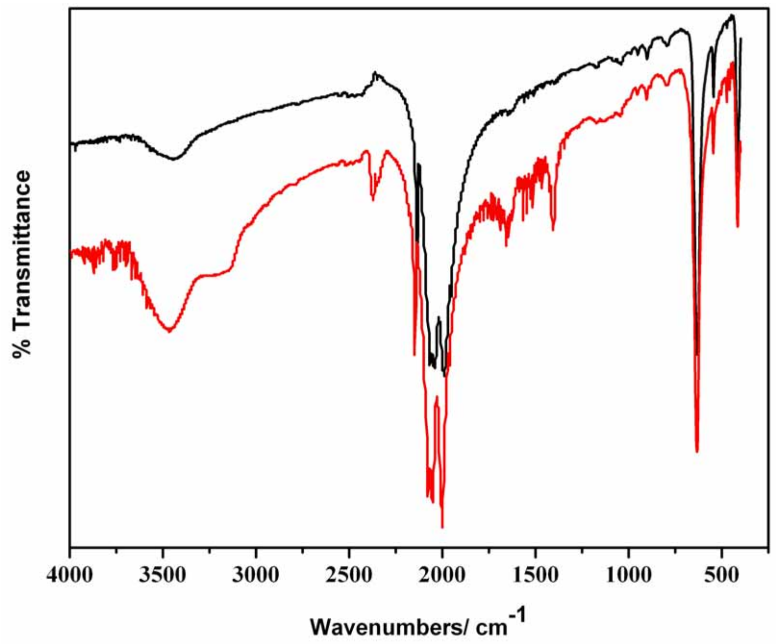

Fig. S9 IR spectra of $Mn(CO)_5Br$ (black) and the IR spectra of $Mn(CO)_5Br$ (red) which was recrystallized in the solution of CH_3CN / Na_2SO_4 (0.4mol·L^{-1}) (1:2, vol) after the catalyses of NO_2^-.

Table S1 The BVS values of all the oxygen atoms except the lattice water molecules in **1**.

Atoms	BVS values	Atoms	BVS values	Atoms	BVS values
O1	2.03	O12	1.72	O25	2.03
O2,	1.71	O13	1.95	O26	2.00
O3	1.64	O14	1.96	O27	1.92
O4	2.00	O15	1.84	O28	1.90
O5	1.67	O18	2.14	O29	1.93
O6	1.61	O19	2.03	O30	1.93
O7	1.80	O21	2.09	O31	2.01
O8	1.96	O22	2.02	O32	1.88
O9	1.67	O23	1.99	O33	1.86
O10	1.85	O24	1.91	O34	1.93
O11	1.86				

Table S2 The BVS values of all the oxygen atoms except the lattice water molecules in **2**.

Atoms	BVS values	Atoms	BVS values	Atoms	BVS values
O1	1.75	O12	1.73	O25	2.10
O2,	1.89	O13	1.79	O26	2.12
O3	1.65	O14	1.77	O27	1.90
O4	1.64	O15	1.94	O28	2.12
O5	1.67	O18	2.03	O29	1.90
O6	1.70	O19	1.99	O30	2.10
O7	1.60	O21	1.80	O31	1.91
O8	1.55	O22	2.02	O32	1.75
O9	1.67	O23	2.01	O33	1.72

O10	1.79	O24	2.03	O34	1.75
O11	1.82				

Table S3 The BVS values of all the W and Ge atoms in **1.**

Atoms	BVS values	Atoms	BVS values	Atoms	BVS values
W1	5.90	W2	6.06	W3	6.01
W4,	6.07	W5	6.06	W6	6.04
W7	6.04	W8	6.01	W9	6.01
Ge	4.00				

Table S4 The BVS values of all the W and Si atoms in **2.**

Atoms	BVS values	Atoms	BVS values	Atoms	BVS values
W1	5.96	W2	6.06	W3	6.09
W4,	6.05	W5	6.21	W6	6.03
W7	5.98	W8	5.89	W9	6.01
Si	3.76				

Table. S5 Summary of [γ-XW_{10}] (X = Ge, Si).

Molar ratio of the TM cation and the precursor	T (°C)	Reaction system	pH value	Phase and transformation
Fe^{3+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 1.118/1	40	1M HAc/KAc buffer	4.8	[K(H_2O)(β-$Fe_2GeW_{10}O_{37}$(OH))(γ-Ge $W_{10}O_{36}$)]$^{12-}$ [1]
Fe^{3+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 2.176/1	45	1M HAc/KAc buffer	4.8	[{β-$Fe_2GeW_{10}O_{37}(OH)_2$}$_2$]$^{12-}$ [1]
Cu^{2+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 1.647/1	50	1 M HAc/KAc buffer	4.8	[$Cu_3(H_2O)$(B-β-GeW_9O_{33}(OH))(B-β-G eW_8O_{30}(OH))]$^{12-}$ [2]
Co^{2+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 1.647/1	50	1M HAc/KAc buffer	4.8	[Co$(H_2O)_2${Co_3(B-β-GeW_9O_{33}(OH))(B-β-GeW_8O_{30}(OH))}$_2$]$^{22-}$ [2]
Mn^{2+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 1.647/1	60	1M HAc/KAc buffer	4.8	[Mn$(H_2O)_2${Mn_3(B-β-GeW_9O_{33}(OH))(B-β-GeW_8O_{30}(OH))}$_2$]$^{22-}$ [2]
Mn^{2+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 1.600/1	room temperature	initial pH 3.8-4.0 aqueous solution	maintained at 4.5	[Rb⊂$(GeW_{10}Mn_2O_{38})_3$]$^{17-}$ [3]
Co^{2+}/[γ-$GeW_{10}O_{36}$]$^{8-}$ = 19.704/1	room temperature	aqueous solution	----	[$Co(H_2O)_6$]$_2$[$Co(H_2O)_3$(α-$GeW_{11}CoO_{38}$)$_3$]$^{6-}$ [4]
Mn^{2+}/[γ-$SiW_{10}O_{36}$]$^{8-}$ = 1.600/1	room temperature	CH_3CN / water	3.8-4.5	[$(CH_3)_3(C_6H_5)N$]$_4$[$(SiO_4)W_{10}Mn^{III}{}_2O_{36}$ H_6]·2CH_3CN·H_2 [5]
Mn^{2+}/[γ-$SiW_{10}O_{36}$]$^{8-}$ = 1.600/1	room temperature	aqueous solution	3.8-4.5	[$(SiO_4)W_{10}Mn^{III}{}_2O_{36}H_6$]$^{4-}$ [6]
Ni^{2+}/[γ-$SiW_{10}O_{36}$]$^{8-}$ = 2.280/1	50	1 M HAc/KAc buffer	4.8	[{β-$SiNi_2W_{10}O_{36}(OH)_2(H_2O)$}$_2$]$^{12-}$ [7]
M^{2+}/[γ-$SiW_{10}O_{36}$]$^{8-}$ = 3.000/1 (M = Mn, Cu, Zn)	90	1 M HAc/NaAc buffer	4.8	[{$SiM_2W_9O_{34}(H_2O)$}$_2$]$^{12-}$ (M = Cu^{II}, Mn^{II}, Zn^{II}) [8]
Mn^{2+}/[γ-$SiW_{10}O_{36}$]$^{8-}$ = 3.000/1	room temperature	aqueous solution	3.9	[$(β_2$-$SiW_{11}MnO_{38}OH)_3$]$^{15-}$ [9]
Ti^{4+}/[γ-$SiW_{10}O_{36}$]$^{8-}$ = 2.200/1	80	aqueous solution	2.0	[{β-$Ti_2SiW_{10}O_{39}$}$_4$]$^{24-}$ [10]

$Co^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 13.194/1	50	NaCl aqueous solution	5.5	$[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(\beta\text{-}SiW_8O_{31})_3^{5-}$ [11]
$Co^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 2.194/1	50	HAc/NaAc buffer	4.8	$[\{Co_3(B\text{-}\beta\text{-}SiW_9O_{33}(OH))(B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2)\}_2]^{22-}$ [12]
$Zr^{4+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 8.778/1	50	HAc/KAc buffer	4.8	$[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$ [13]
$Zr^{4+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 4.389/1	50	HAc/KAc buffer	4.8	$[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$ [13]
$Fe^{3+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 2.030/1	room temperature	aqueous solution	4.3	$[\{Fe_2(OH)_3(H_2O)_2\}_3(\gamma\text{-}SiW_{10}O_{36})_3]^{15-}$ [14]
$Fe^{3+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 2.030/1	room temperature	0.5 M HAc/KAc buffer	4.7	$[\{Fe(OH)(OAc)\}_4(\gamma\text{-}SiW_{10}O_{36})_2]^{12-}$ [15]
$Mn^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 1.993/1	room temperature	methanol-acetonitrile solution	----	$[\{(\gamma\text{-}SiW_{10}O_{36})Mn_2(OH)_2(N_3)_{0.5}(H_2O)_{0.5}\}_2(\mu\text{-}1,3\text{-}N_3)]^{10-}$ [16]
$Cu^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 1.993/1	room temperature	methanol-acetonitrile solution	----	$[(\gamma\text{-}SiW_{10}O_{36})_2Cu_4(\mu\text{-}1,1,1\text{-}N_3)_2(\mu\text{-}1,1\text{-}N_3)_2]^{12-}$ [16]
$Co^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 2.077/1	room temperature	aqueous solution	5	$[\{(B\text{-}\beta\text{-}SiW_9O_{33}(OH))(\beta\text{-}SiW_8O_{29}(OH)_2)Co_3(H_2O)\}_2Co(H_2O)_2]^{20-}$ [17]
$Co^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 0.515/1	room temperature	aqueous solution	5	$[Co1.5(HO)7)][(\gamma\text{-}SiW_{10}O_{36})(b\text{-}SiW_8O_{30}(OH))Co_4(OH)(H_2O)_7]^{7-}$ [17]
$Ni^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 6.818/1	100	aqueous solution	the end pH 5.8	$\{[Ni(dap)_2(H_2O)]_2[Ni(dap)_2]_2[Ni_4(Hdap)_2(\alpha\text{-}B\text{-}HSiW_9O_{34})_2]\}\cdot 7H_2O$ [18]
$Fe^{3+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 2.030/1	room temperature	aqueous solution	1.7	$[\beta\text{-}SiFe_2W_{10}O_{36}(OH)_2(H_2O)Cl]^{5-}$ [19]
$Mn^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 5.112/1	room temperature	1 M HAc/NaAc buffer	5.0	$\{[Mn(H_2O)_3]_2[Mn(H_2O)_2][(B\text{-}\beta\text{-}SiW_9O_{33}(OH))Mn_3(H_2O)(B\text{-}\beta\text{-}SiW_8O_{30}(OH))]_2\}^{18-}$ [4]
$Cd^{2+}/[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ = 10.337/1	room temperature	1 M HAc/NaAc buffer	5.0	$[Cd(H_2O)_3]_2[Cd_4(H_2O)_2(B\text{-}\alpha\text{-}SiW_9O_{34})_2]^{8-}$ [4]

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