Probing the self-assembly mechanism of lanthanide-containing sandwich-type silicotungstates $[\{Ln(H_2O)_n\}_2\{Mn_4(B\text{-}\alpha\text{-}SiW_9O_{34})_2(H_2O)_2\}]^{6-}$ using time-resolved mass spectrometry and X-ray crystallography

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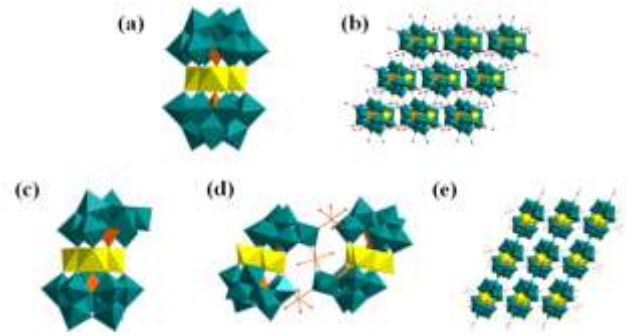

Figure S1 Polyhedral and ball-and-stick representations of compounds **6** and **7**: (a) the coordination environment of $[Mn_4(B\text{-}\alpha\text{-}SiW_9O_{34})_2(H_2O)_2]^{12-}$ in **6**; (b) the 2D network packing arrangement displaying of $[Mn_4(B\text{-}\alpha\text{-}SiW_9O_{34})_2(H_2O)_2]^{12-}$ in **6**; (c) the coordination environment of $[Mn_4(B\text{-}\alpha\text{-}SiW_9O_{34})_2(H_2O)_2]^{12-}$ in **3**; (d) the coordination environment of Mn^{2+} in **7;** (e) the 2D network packing arrangement displaying of $[\{Mn(H_2O)_3\}_2\{Mn(H_2O)_2\}\{Mn_3(B\text{-}\beta\text{-}SiW_9O_{33}(OH))(B\text{-}\beta\text{-}SiW_8O_{30}(OH))(H_2O)\}_2]^{18-}$ in **7**. Color scheme: W = teal; Mn = yellow; O = red; Si = orange.

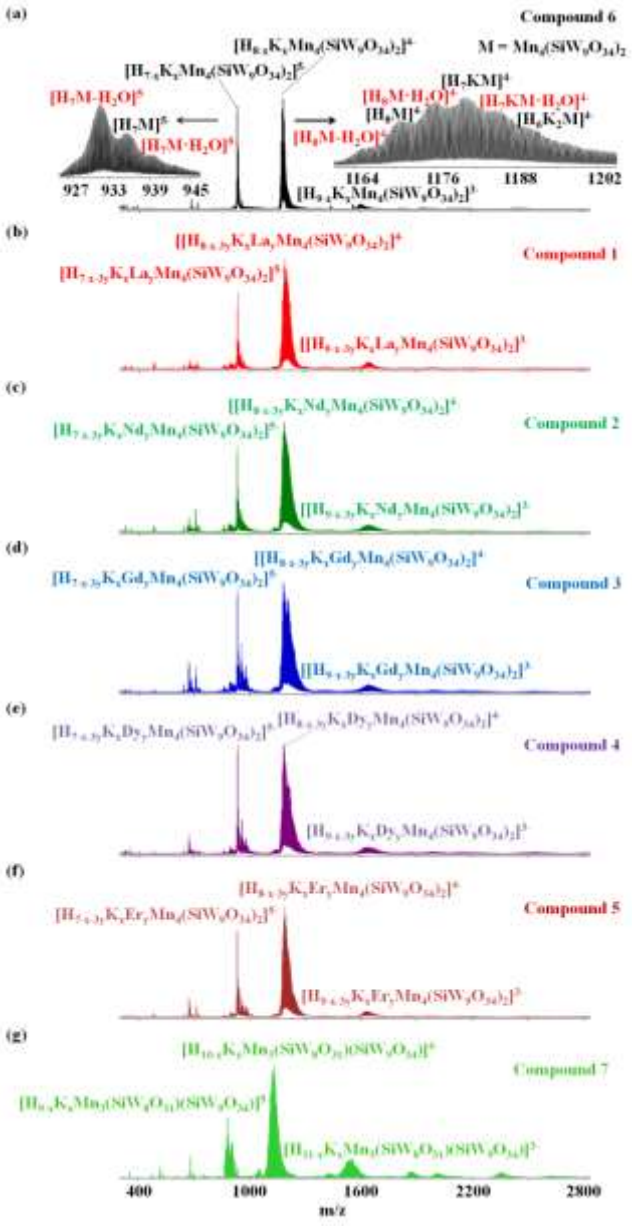

Figure S2 ESI-MS spectra of crystals **1** – **7** redissolved in water: (a) crystal **6**; (b) crystal **1**; (c) crystal **2**; (d) crystal **3**; (e) crystal **4**; (f) crystal **5**; (g) crystal **7**.

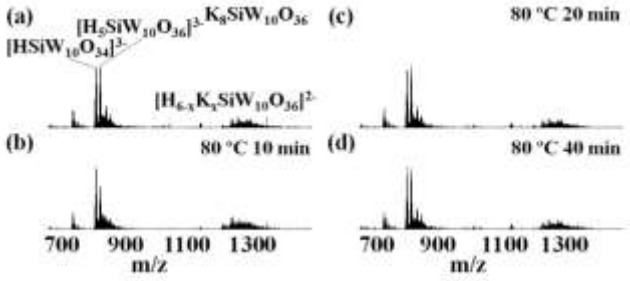

Figure S3 Real-time ESI-MS monitoring on an aqueous solution of pure $K_8SiW_{10}O_{36}$ upon heating at 80 °C for different time intervals: (a) t = 0 min; (b) 10 min; (c) 20 min and (d) 40 min, indicating that no speciation change occurred in the isolated $\{\gamma\text{-}SiW_{10}\}$ solution.

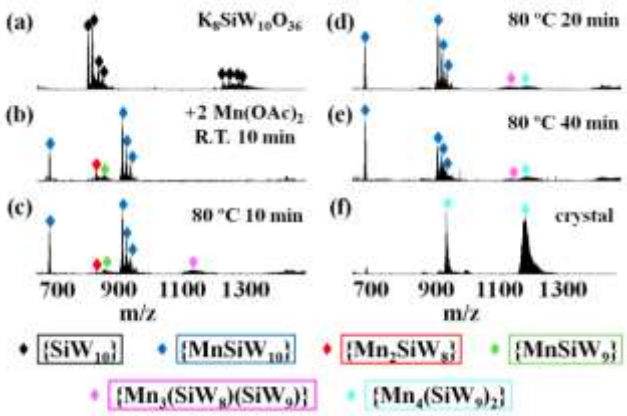

Figure S4 Real-time ESI-MS monitoring on the synthetic process of compound **6**: (a) $K_8SiW_{10}O_{36}$ dissolved in water; (b) adding 2 equiv. $Mn(OAc)_2$ to the {γ-SiW_{10}} solution with stirring for 10 min at RT; (c) – (e) heating the solution (b) at 80 °C for different time intervals; (f) ESI-MS spectrum of crystal **6** redissolved in water.

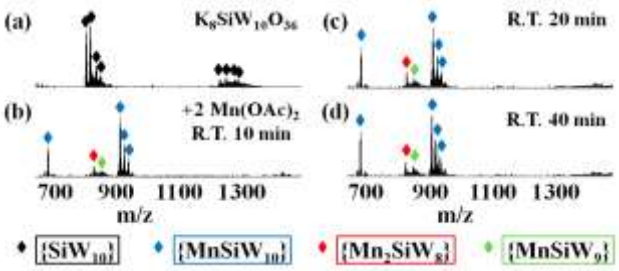

Figure S5 Real-time ESI-MS monitoring on the reaction of $K_8SiW_{10}O_{36}$ with $Mn(OAc)_2$ at RT: (a) $K_8SiW_{10}O_{36}$ dissolved in water; (b) – (d) adding 2 equiv. $Mn(OAc)_2$ to the $\{\gamma\text{-}SiW_{10}\}$ solution with stirring for different time intervals.

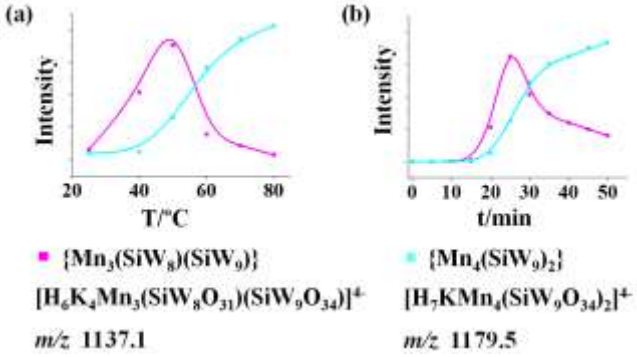

Figure S6 Graphs showing peak intensities of the intermediate species $\{Mn_3(SiW_8)(SiW_9)\}$ ($[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$ at *m*/*z* 1137.1) and product species $\{Mn_4(SiW_9)_2\}$ ($[H_7Mn_4(SiW_9O_{34})_2]^{4-}$ at *m*/*z* 1179.5) against (a) reaction temperature (T) at t = 50 min and (b) reaction time (t) of ESI-MS data acquisition during the reaction of $\{\gamma\text{-}SiW_{10}\}$ + $Mn(OAc)_2$.

Table S1. ESI-MS envelopes for species found in the reaction of SiW_{10}+Mn^{2+}+Ln^{3+} at 80 °C.

Reaction solution	Envelope Assignment	m/z (obs) (%)
SiW_{10}	$[HSiW_{10}O_{34}]^{3-}$	804.1 (96)
	$[H_5SiW_{10}O_{36}]^{3-}$	816.1 (100)
	$[H_4KSiW_{10}O_{36}\bullet H_2O]^{3-}$	834.7 (36)
	$[H_3K_2SiW_{10}O_{36}\bullet H_2O]^{3-}$	847.4 (10)
	$[H_6SiW_{10}O_{36}]^{2-}$	1224.6 (14)
	$[H_5KSiW_{10}O_{36}]^{2-}$	1243.6 (16)
	$[H_4K_2SiW_{10}O_{36}\bullet H_2O]^{2-}$	1273.6 (14)
	$[H_3K_3SiW_{10}O_{36}]^{2-}$	1281.6 (13)
SiW_{10} + $Mn(OAc)_2$ R.T. 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (48)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (21)
	$[K_6MnSiW_9O_{34}(OH)\bullet H_2O]^{3-}$	850.4 (11)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (31)
SiW_{10} + $Mn(OAc)_2$ + $Gd(NO_3)_3$ 80 °C 10 min	$[K_3GdMnSiW_{10}O_{36}(OH)_4]^{4-}$	709.8 (100)
	$[K_6MnSiW_9O_{34}(OH)\bullet H_2O]^{3-}$	850.4 (11)
	$[Na_3K_3GdSiW_{10}O_{36}(OH)_3]^{3-}$	937.7 (62)
	$[Na_2K_4GdSiW_{10}O_{36}(OH)_4]^{3-}$	956.0 (50)
	$[Na_3K_4GdSiW_{10}O_{36}(OH)_5]^{3-}$	970.0 (17)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (2)
SiW_{10} + $Mn(OAc)_2$ + $Gd(NO_3)_3$ 80 °C 20 min	$[K_3GdMnSiW_{10}O_{36}(OH)_4]^{4-}$	709.8 (100)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (15)
	$[Na_3K_3GdSiW_{10}O_{36}(OH)_3]^{3-}$	937.7 (71)
	$[Na_2K_4GdSiW_{10}O_{36}(OH)_4]^{3-}$	956.0 (65)
	$[Na_3K_4GdSiW_{10}O_{36}(OH)_5]^{3-}$	970.0 (20)

	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$ $[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1137.1 (2) 1174.6 (1)
SiW_{10} + $Mn(OAc)_2$ + $Gd(NO_3)_3$ 80 °C 40 min	$[K_3GdMnSiW_{10}O_{36}(OH)_4]^{4-}$ $[K_6MnSiW_9O_{34}(OH) \cdot 2H_2O]^{3-}$ $[Na_3K_3GdSiW_{10}O_{36}(OH)_3]^{3-}$ $[Na_2K_4GdSiW_{10}O_{36}(OH)_4]^{3-}$ $[Na_3K_4GdSiW_{10}O_{36}(OH)_5]^{3-}$ $[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	709.8 (100) 856.4 (15) 937.7 (62) 956.0 (50) 970.0 (17) 1174.6 (2)
Crystal 3	$[H_{7-x-3y}K_xGd_yMn_4(SiW_9O_{34})_2]^{5-}$ $[H_{8-x-3y}K_xGd_yMn_4(SiW_9O_{34})_2]^{4-}$	932.3 – 989.6 (79) 1165.6 – 1247.3 (100)

Table S2. ESI-MS envelopes for species found in the reaction of SiW_{10}+Mn^{2+} at 80 °C.

Reaction solution	Envelope Assignment	m/z (obs) (%)
SiW_{10}	$[HSiW_{10}O_{34}]^{3-}$	804.1 (96)
	$[H_5SiW_{10}O_{36}]^{3-}$	816.1 (100)
	$[H_4KSiW_{10}O_{36}\bullet H_2O]^{3-}$	834.7 (36)
	$[H_3K_2SiW_{10}O_{36}\bullet H_2O]^{3-}$	847.4 (10)
	$[H_6SiW_{10}O_{36}]^{2-}$	1224.6 (14)
	$[H_5KSiW_{10}O_{36}]^{2-}$	1243.6 (16)
	$[H_4K_2SiW_{10}O_{36}\bullet H_2O]^{2-}$	1273.6 (14)
	$[H_3K_3SiW_{10}O_{36}]^{2-}$	1281.6 (13)
SiW_{10} + $Mn(OAc)_2$ R.T. 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (48)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (21)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (11)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (31)
SiW_{10} + $Mn(OAc)_2$ 80 °C 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (67)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (3)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (7)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (53)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (25)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (5)
SiW_{10} + $Mn(OAc)_2$ 80 °C 20 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (68)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (54)

	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (28)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (3)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4}$	1174.6 (4)
SiW_{10} + $Mn(OAc)_2$ 80 °C 40 min	$[K_4MnSiW_{10}O_{36}(OH)_2 \bullet 2H_2O]^{4-}$	681.0 (69)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2 \bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3 \bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (26)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (1)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4}$	1174.6 (6)
crystal 6	$[H_{7-x}K_xMn_4(SiW_9O_{34})_2]^{5-}$	932.3 – 943.4 (98)
	$[H_{8-x}K_xMn_4(SiW_9O_{34})_2]^{4-}$	1165.6 – 1193.8 (100)

Table S3. ESI-MS envelopes for species found in the reaction of SiW_{10}+Mn^{2+} at 50 °C.

Reaction solution	Envelope Assignment	m/z (obs) (%)
SiW_{10}	$[HSiW_{10}O_{34}]^{3-}$	804.1 (96)
	$[H_5SiW_{10}O_{36}]^{3-}$	816.1 (100)
	$[H_4KSiW_{10}O_{36}\bullet H_2O]^{3-}$	834.7 (36)
	$[H_3K_2SiW_{10}O_{36}\bullet H_2O]^{3-}$	847.4 (10)
	$[H_6SiW_{10}O_{36}]^{2-}$	1224.6 (14)
	$[H_5KSiW_{10}O_{36}]^{2-}$	1243.6 (16)
	$[H_4K_2SiW_{10}O_{36}\bullet H_2O]^{2-}$	1273.6 (14)
	$[H_3K_3SiW_{10}O_{36}]^{2-}$	1281.6 (13)
SiW_{10} + $Mn(OAc)_2$ R.T. 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (48)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (21)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (11)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (31)
SiW_{10} + $Mn(OAc)_2$ 50 °C 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (76)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (3)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (30)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (1)
SiW_{10} + $Mn(OAc)_2$ 50 °C 20 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (72)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (50)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (28)

	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (2)
SiW_{10} + $Mn(OAc)_2$ 50 °C 40 min	$[K_4MnSiW_{10}O_{36}(OH)_2 \bullet 2H_2O]^{4-}$	681.0 (69)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2 \bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3 \bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (26)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (4)
crystal 7	$[H_{9-x}K_xMn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	878.9 – 901.9 (54)
	$[H_{1o-x}K_xMn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1103.8 – 1161.3 (100)

Table S4. ESI-MS envelopes for species found in the reaction of SiW_{10}+Mn^{2+} at room temperature.

Reaction solution	Envelope Assignment	m/z (obs) (%)
SiW_{10}	$[HSiW_{10}O_{34}]^{3-}$	804.1 (96)
	$[H_5SiW_{10}O_{36}]^{3-}$	816.1 (100)
	$[H_4KSiW_{10}O_{36}•H_2O]^{3-}$	834.7 (36)
	$[H_3K_2SiW_{10}O_{36}•H_2O]^{3-}$	847.4 (10)
	$[H_6SiW_{10}O_{36}]^{2-}$	1224.6 (14)
	$[H_5KSiW_{10}O_{36}]^{2-}$	1243.6 (16)
	$[H_4K_2SiW_{10}O_{36}•H_2O]^{2-}$	1273.6 (14)
	$[H_3K_3SiW_{10}O_{36}]^{2-}$	1281.6 (13)
SiW_{10} + $Mn(OAc)_2$ R.T. 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (48)
	$[K_7Mn_2SiW_8O_{31}(OH)_4•2H_2O]^{3-}$	827.4 (21)
	$[K_6MnSiW_9O_{34}(OH)•2H_2O]^{3-}$	856.4 (11)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (31)
SiW_{10} + $Mn(OAc)_2$ R.T. 20 min	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (67)
	$[K_7Mn_2SiW_8O_{31}(OH)_4•2H_2O]^{3-}$	827.4 (23)
	$[K_6MnSiW_9O_{34}(OH)•2H_2O]^{3-}$	856.4 (17)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (53)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3--}$	935.7 (25)
SiW_{10} + $Mn(OAc)_2$	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (67)
	$[K_7Mn_2SiW_8O_{31}(OH)_4•2H_2O]^{3-}$	827.4 (25)
	$[K_6MnSiW_9O_{34}(OH)•2H_2O]^{3-}$	856.4 (20)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)

R.T. 40 min	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3 \bullet H_2O]^{3-}$ $[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	923.0 (53) 935.7 (25)

Table S5. ESI-MS envelopes for species found in the reaction of SiW_{10}+Mn^{2+} under gradual increased temperature.

Reaction solution	Envelope Assignment	m/z (obs) (%)
SiW_{10}	$[HSiW_{10}O_{34}]^{3-}$	804.1 (96)
	$[H_5SiW_{10}O_{36}]^{3-}$	816.1 (100)
	$[H_4KSiW_{10}O_{36}\bullet H_2O]^{3-}$	834.7 (36)
	$[H_3K_2SiW_{10}O_{36}\bullet H_2O]^{3-}$	847.4 (10)
	$[H_6SiW_{10}O_{36}]^{2-}$	1224.6 (14)
	$[H_5KSiW_{10}O_{36}]^{2-}$	1243.6 (16)
	$[H_4K_2SiW_{10}O_{36}\bullet H_2O]^{2-}$	1273.6 (14)
	$[H_3K_3SiW_{10}O_{36}]^{2-}$	1281.6 (13)
SiW_{10} + $Mn(OAc)_2$ R.T. 40 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (67)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (25)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (20)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (53)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (25)
SiW_{10} + $Mn(OAc)_2$ 50 °C 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (76)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (3)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (5)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2\bullet 3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3\bullet H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (30)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (1)
SiW_{10} + $Mn(OAc)_2$	$[K_4MnSiW_{10}O_{36}(OH)_2\bullet 2H_2O]^{4-}$	681.0 (72)
	$[K_7Mn_2SiW_8O_{31}(OH)_4\bullet 2H_2O]^{3-}$	827.4 (1)
	$[K_6MnSiW_9O_{34}(OH)\bullet 2H_2O]^{3-}$	856.4 (1)

50 °C 20 min	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (50)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (28)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (2)
SiW_{10} + $Mn(OAc)_2$ 50 °C 40 min	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (69)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (54)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (26)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (4)
SiW_{10} + $Mn(OAc)_2$ 80 °C 10 min	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (69)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (50)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (21)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (4)
	$[H_8Mn_4(SiW_9O_{34})_2·H_2O]^{4-}$	1174.6 (1)
SiW_{10} + $Mn(OAc)_2$ 80 °C 20 min	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (69)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (52)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (23)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	1137.1 (2)
	$[H_8Mn_4(SiW_9O_{34})_2·H_2O]^{4-}$	1174.6 (3)
SiW_{10} + $Mn(OAc)_2$ 80 °C 40 min	$[K_4MnSiW_{10}O_{36}(OH)_2•2H_2O]^{4-}$	681.0 (65)
	$[Na_3K_2MnSiW_{10}O_{36}(OH)_2•3H_2O]^{3-}$	911.1 (100)
	$[Na_2K_4MnSiW_{10}O_{36}(OH)_3•H_2O]^{3-}$	923.0 (55)
	$[Na_2K_5MnSiW_{10}O_{36}(OH)_4]^{3-}$	935.7 (27)
	$[H_8Mn_4(SiW_9O_{34})_2·H_2O]^{4-}$	1174.6 (5)

Table S6. ESI-MS envelopes for species crystal **1 – 7** re-dissolved in water.

Solution	Envelope Assignment	m/z (obs) (%)
crystal 1	$[H_7Mn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	932.3 (74)
	$[H_7Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	939.5 (23)
	$[H_4LaMn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	966.7 (74)
	$[H_8Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1165.6 (20)
	$[H_8Mn_4(SiW_9O_{34})_2]^{4-}$	1170.1 (27)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1174.6 (64)
	$[H_7KMn_4(SiW_9O_{34})_2]^{4-}$	1179.6 (74)
	$[H_7KMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1184.1 (97)
	$[H_6K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1189.3 (100)
	$[H_5K_3Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1193.8 (92)
	$[H_5K_3Mn_4(SiW_9O_{34})_2]^{4-}$	1198.8 (93)
	$[H_5LaMn_4(SiW_9O_{34})_2]^{4-}$	1204.1 (81)
	$[H_5LaMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1208.6 (73)
	$[H_4KLaMn_4(SiW_9O_{34})_2]^{4-}$	1213.6 (62)
	$[H_4KLaMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1218.1 (48)
	$[H_3K_2LaMn_4(SiW_9O_{34})_2]^{3-}$	1631.4 (6)
	$[H_3K_3LaMn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1650.7 (6)
crystal 2	$[H_7Mn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	932.3 (78)
	$[H_7Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	939.5 (27)
	$[H_4NdMn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	960.5 (8)
	$[H_8Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1165.6 (21)
	$[H_8Mn_4(SiW_9O_{34})_2]^{4-}$	1170.1 (31)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1174.6 (65)
	$[H_7KMn_4(SiW_9O_{34})_2]^{4-}$	1179.6 (86)
	$[H_7KMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1184.1 (99)

	$[H_6K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1189.3 (100)
	$[H_5K_3Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1193.8 (89)
	$[H_5K_3Mn_4(SiW_9O_{34})_2]^{4-}$	1198.8 (80)
	$[H_5NdMn_4(SiW_9O_{34})_2]^{4-}$	1205.6 (71)
	$[H_5NdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1210.1 (67)
	$[H_4KNdMn_4(SiW_9O_{34})_2]^{4-}$	1215.1 (65)
	$[H_4KNdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1219.6 (50)
	$[H_3K_2NdMn_4(SiW_9O_{34})_2]^{4-}$	1224.6 (48)
	$[H_3K_2NdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1229.1 (34)
	$[H_4K_2NdMn_4(SiW_9O_{34})_2]^{3-}$	1633.7 (5)
	$[H_3K_3NdMn_4(SiW_9O_{34})_2]^{3-}$	1646.4 (6)
crystal 3	$[H_7Mn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	932.3 (79)
	$[H_7Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	939.5 (29)
	$[H_5K_2Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	951.3 (36)
	$[H_4GdMn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	963.3 (20)
	$[H_3KGdMn_4(SiW_9O_{34})_2]^{5-}$	974.5 (17)
	$[H_2K_2GdMn_4(SiW_9O_{34})_2]^{5-}$	982.1 (15)
	$[HK_3GdMn_4(SiW_9O_{34})_2]^{5-}$	989.6 (6)
	$[H_8Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1165.6 (12)
	$[H_8Mn_4(SiW_9O_{34})_2]^{4-}$	1170.1 (18)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1174.6 (48)
	$[H_7KMn_4(SiW_9O_{34})_2]^{4-}$	1179.6 (73)
	$[H_7KMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1184.1 (93)
	$[H_6K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1189.3 (99)
	$[H_5K_3Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1193.8 (100)
	$[H_5K_3Mn_4(SiW_9O_{34})_2]^{4-}$	1198.8 (90)
	$[H_5GdMn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1204.3 (88)

	$[H_5GdMn_4(SiW_9O_{34})_2]^{4-}$	1208.8 (86)
	$[H_5GdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1213.3 (86)
	$[H_4KGdMn_4(SiW_9O_{34})_2]^{4-}$	1218.3 (78)
	$[H_4KGdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1222.8 (61)
	$[H_3K_2GdMn_4(SiW_9O_{34})_2]^{4-}$	1227.8 (55)
	$[H_2Gd_2Mn_4(SiW_9O_{34})_2]^{4-}$	1247.3 (33)
	$[H_4K_2GdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1644.4 (6)
	$[H_3K_3GdMn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1657.1 (5)
	$[H_3Gd_2Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1670.4 (4)
crystal 4	$[H_7Mn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	932.3 (84)
	$[H_7Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	939.5 (28)
	$[H_6KMn_4(SiW_9O_{34})_2]^{5-}$	943.5 (25)
	$[H_5K_2Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	951.3 (20)
	$[H_4DyMn_4(SiW_9O_{34})_2] - H_2O^{5-}$	964.3 (13)
	$[H_4DyMn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	979.1 (10)
	$[H_3KDyMn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	986.7 (8)
	$[H_8Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1165.6 (13)
	$[H_8Mn_4(SiW_9O_{34})_2]^{4-}$	1170.1 (22)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1174.6 (55)
	$[H_7KMn_4(SiW_9O_{34})_2]^{4-}$	1179.6 (77)
	$[H_7KMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1184.1 (95)
	$[H_6K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1189.3 (100)
	$[H_5K_3Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1193.8 (94)
	$[H_5K_3Mn_4(SiW_9O_{34})_2]^{4-}$	1198.8 (82)
	$[H_5DyMn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1205.6 (73)
	$[H_5DyMn_4(SiW_9O_{34})_2]^{4-}$	1210.1 (70)
	$[H_5DyMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1214.6 (67)

	$[H_4KDyMn_4(SiW_9O_{34})_2]^{4-}$	1219.6 (58)
	$[H_4KDyMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1224.6 (48)
	$[H_3K_2DyMn_4(SiW_9O_{34})_2]^{4-}$	1229.1 (37)
	$[H_2Dy_2Mn_4(SiW_9O_{34})_2]^{4-}$	1250.1 (17)
	$[H_5KDyMn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1632.4 (6)
	$[H_4K_2DyMn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1645.1 (6)
	$[H_3K_3Dy_2Mn_4(SiW_9O_{34})_2]^{3-}$	1651.7 (5)
crystal 5	$[H_7Mn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	932.3 (79)
	$[H_7Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	939.5 (27)
	$[H_6KMn_4(SiW_9O_{34})_2]^{5-}$	943.5 (26)
	$[H_5K_2Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	954.9 (17)
	$[H_4ErMn_4(SiW_9O_{34})_2] - H_2O^{5-}$	965.7 (9)
	$[H_3KErMn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	980.1 (10)
	$[H_2K_2ErMn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	987.7 (8)
	$[H_8Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1165.6 (11)
	$[H_8Mn_4(SiW_9O_{34})_2]^{4-}$	1170.1 (19)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1174.6 (50)
	$[H_7KMn_4(SiW_9O_{34})_2]^{4-}$	1179.6 (76)
	$[H_7KMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1184.1 (89)
	$[H_6K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1189.3 (100)
	$[H_5K_3Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1193.8 (90)
	$[H_5K_3Mn_4(SiW_9O_{34})_2]^{4-}$	1198.8 (75)
	$[H_5ErMn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1206.8 (60)
	$[H_5ErMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1215.8 (51)
	$[H_4KErMn_4(SiW_9O_{34})_2]^{4-}$	1220.8 (41)
	$[H_4KErMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1225.3 (30)
	$[H_3K_2ErMn_4(SiW_9O_{34})_2]^{4-}$	1234.8 (20)

	$[H_3K_2ErMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1244.8 (18)
	$[H_2Er_2Mn_4(SiW_9O_{34})_2]^{4-}$	1252.3 (13)
	$[HKEr_2Mn_4(SiW_9O_{34})_2]^{4-}$	1261.8 (9)
	$[H_5KErMn_4(SiW_9O_{34})_2 \cdot H_2O]^{3-}$	1634.1 (5)
	$[H_4K_2ErMn_4(SiW_9O_{34})_2]^{3-}$	1640.7 (4)
	$[H_3K_3ErMn_4(SiW_9O_{34})_2]^{3-}$	1653.4 (4)
crystal 6	$[H_7Mn_4(SiW_9O_{34})_2 - H_2O]^{5-}$	932.3 (98)
	$[H_7Mn_4(SiW_9O_{34})_2]^{5-}$	935.8 (48)
	$[H_7Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{5-}$	939.5 (22)
	$[H_6KMn_4(SiW_9O_{34})_2]^{5-}$	943.4 (9)
	$[H_8Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1165.6 (52)
	$[H_8Mn_4(SiW_9O_{34})_2]^{4-}$	1170.1 (67)
	$[H_8Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1174.6 (90)
	$[H_7KMn_4(SiW_9O_{34})_2]^{4-}$	1179.6 (100)
	$[H_7KMn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1184.1 (87)
	$[H_6K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1189.3 (43)
	$[H_5K_3Mn_4(SiW_9O_{34})_2 - H_2O]^{4-}$	1193.8 (30)
	$[H_7K_2Mn_4(SiW_9O_{34})_2]^{4-}$	1586.1 (7)
	$[H_7K_2Mn_4(SiW_9O_{34})_2 \cdot H_2O]^{4-}$	1592.1 (8)
	$[H_6K_3Mn_4(SiW_9O_{34})_2]^{4-}$	1598.7 (7)
crystal 7	$[H_9Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	878.9 (52)
	$[H_6KMn_3(SiW_8O_{30})(SiW_9O_{34})]^{5-}$	882.9 (54)
	$[H_8KMn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	886.5 (39)
	$[H_5K_2Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{5-}$	890.7 (28)
	$[H_7K_2Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	894.3 (19)
	$[H_4K_3Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{5-}$	898.3 (23)
	$[H_6K_3Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{5-}$	901.9 (31)

	$[H_7KMn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1103.8 (39)
	$[H_9KMn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1108.3 (59)
	$[H_6K_2Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1113.6 (81)
	$[H_8K_2Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1118.1 (75)
	$[H_5K_3Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1123.1 (90)
	$[H_7K_3Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1127.6 (91)
	$[H_4K_4Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1132.6 (95)
	$[H_6K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1137.1 (100)
	$[H_3K_5Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1142.1 (71)
	$[H_5K_5Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1146.6 (65)
	$[H_2K_6Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1151.6 (51)
	$[H_4K_6Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{4-}$	1156.1 (41)
	$[HK_7Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{4-}$	1161.3 (34)
	$[H_7Mn_3(SiW_8O_{30})(SiW_9O_{33})]^{3-}$	1453.1 (6)
	$[H_7K_4Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{3-}$	1516.1 (14)
	$[H_3K_6Mn_3(SiW_8O_{30})(SiW_9O_{34})]^{3-}$	1535.4 (17)
	$[H_4K_7Mn_3(SiW_8O_{31})(SiW_9O_{34})]^{3-}$	1554.4 (19)