Supporting Information

Synthesis, crystal structure, electrochemistry and magnetism of a Mn^{III}-substituted trilacunary Keggin tungstosilicate

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Crystal structure:

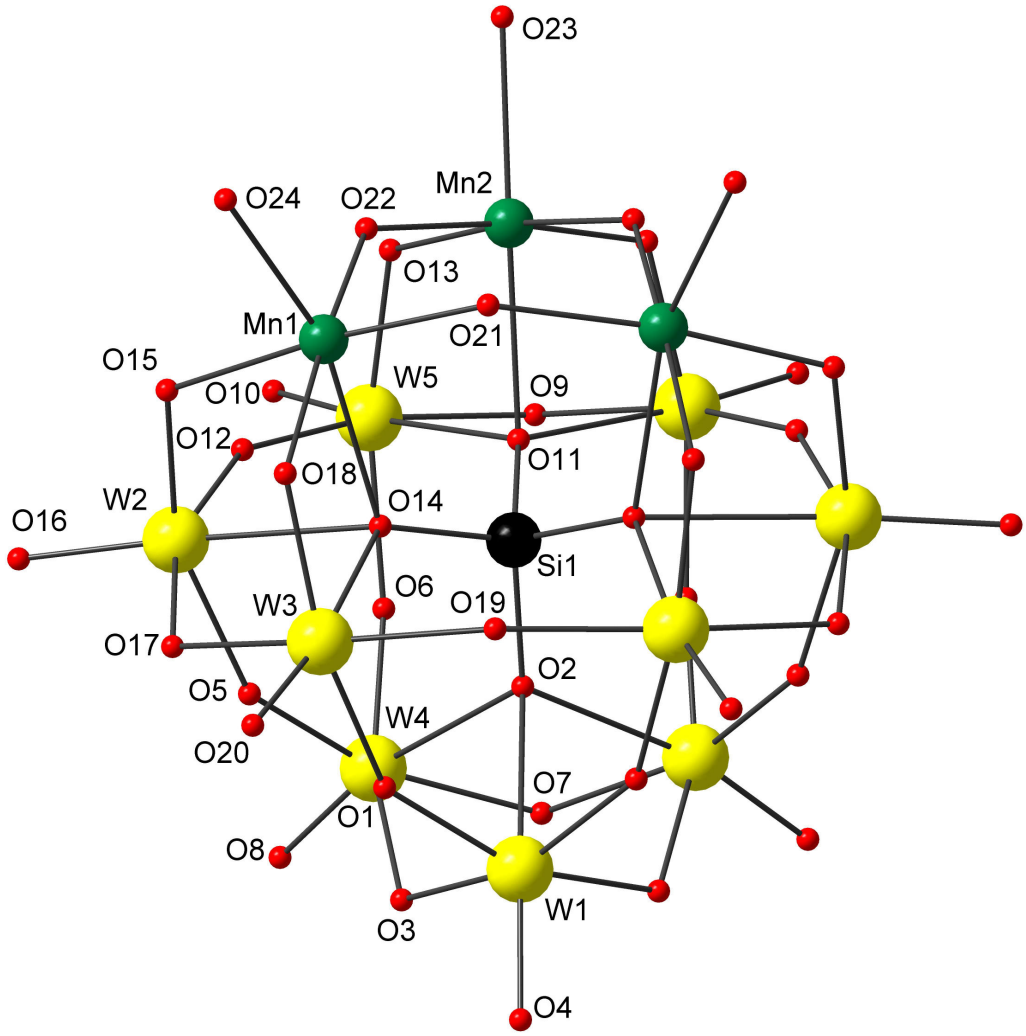
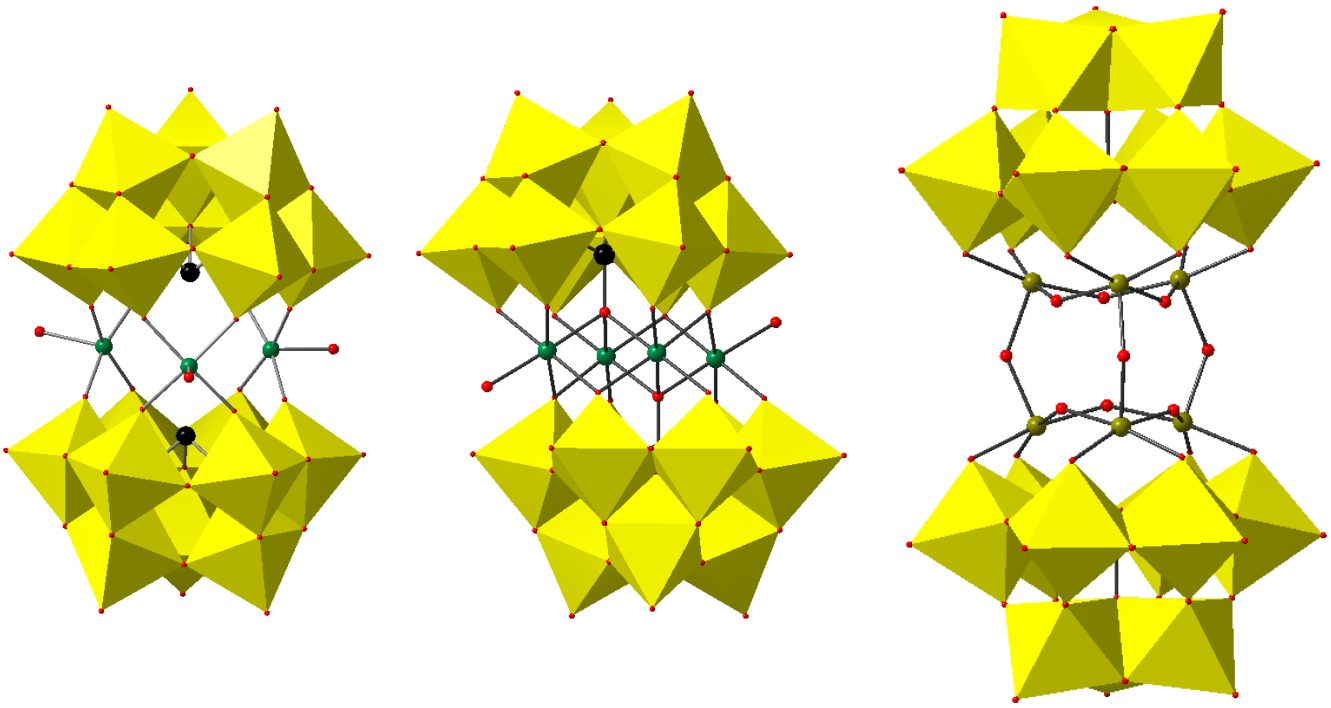


Figure S1. The labeling scheme of the POM anion in **1**.



a b c

Figure S2. Most common structures of TMSPs based on trilacunary Keggin anions:

a) $[(M(H_2O))_3(XW_9O_{33})_2]^{n-}$; b) $[M_4(H_2O)_2(XW_9O_{34})_2]^{m-}$; c) $[(M_3(OH)_3XW_9O_{34})_2(OH)_3]^{p-}$

Coordination geometries of potassium atoms.

Three different coordination environments around potassium ions can be distinguished in the crystal structure of **1**. The coordination sphere of the K1 cation (Fig. S3a) is occupied by one water molecule coordinated to a manganese ion, two crystal lattice water molecules, and three terminal oxygen atoms of three different POM anions forming a distorted pentagonal pyramid with one of POM oxygen atom in the top. The K1–O distances range from 2.764(7) to 3.106(8) Å. The K2 atom (Fig. S3b) is situated between eight corners sharing oxygen atoms of two manganese tungstosilicate anions and has a slightly distorted tetragonal prismatic geometry with K2–O distances ranging from 2.819(6) to 2.986(7) Å. The K3 cation (Fig. S3c) is seven-coordinated, being surrounded in an irregular way by three terminal oxygen atoms of three different POM anions, a terminal water molecule, the bridging oxo-groups of a fourth POM anion, and two lattice water molecules, which are bridging two K3 cations. The K3–O distances fall into the range of 2.66(2)–2.94(1) Å. Totally 14 K^+ ions (4 of the K1 type, 2 of the K2 type and 8 of the K3 type; Fig. S3d) surround each $[Mn_3(OH)_3(H_2O)_3SiW_9O_{34}]^{5-}$ anion forming a complex 3D network.

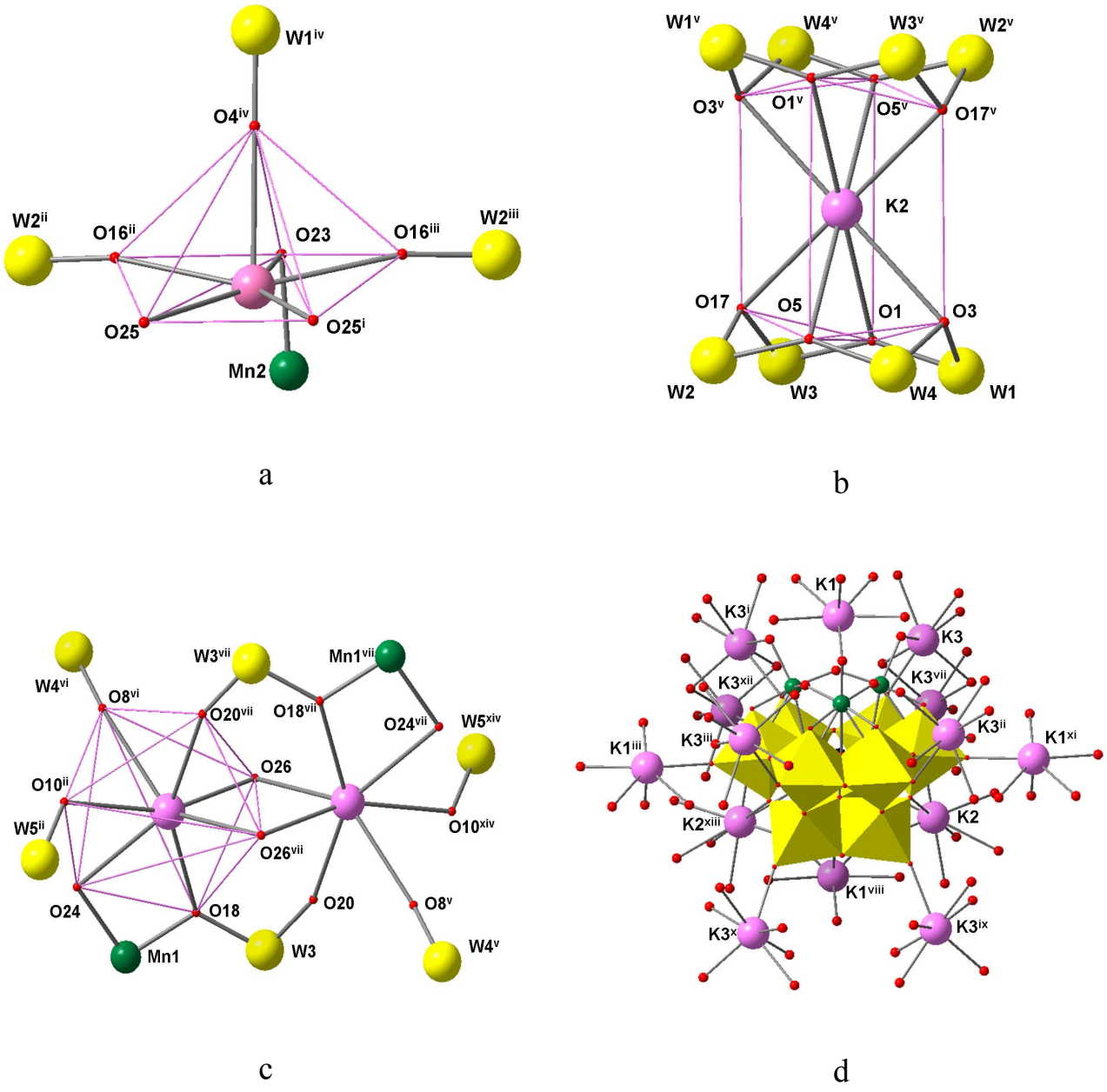


Figure S3. A distorted pentagonal pyramidal coordination environment of K1 (**a**). A distorted tetragonal prismatic geometry of K2 (**b**). An irregular coordination environment of K3 (**c**). 14 potassium ions surround the $[Mn_3(OH)_3(H_2O)_3SiW_9O_{34}]^{-5}$ anion (**d**).

Symmetry codes:

(i) x, 0.5-y, z; (ii) 1-x, -y, 1-z; (iii) 1-x, 0.5+y, 1-z; (iv) -1+x, y, -1+z; (v) 2-x, -y, 2-z; (vi) -1+x, y, z; (vii) 1-x, -y, 2-z; (viii) 1+x, y, 1+z; (ix) 1+x, y, z; (x) 1+x, 0.5-y, z; (xi) 1-x, -0.5+y, 1-z; (xii) 1-x, 0.5+y, 2-z; (xiii) 2-x, 0.5+y, 2-z; (xiv) x, y, 1+z.

Table S1. Selected bond lengths

Mn1—O21	1.915(4)	W4—O3	1.946(7)
Mn1—O22	1.931(8)	W4—O2	2.313(6)
Mn1—O15	1.938(7)	W5—O10	1.714(9)
Mn1—O18	1.941(7)	W5—O13	1.851(7)
Mn1—O24	2.142(8)	W5—O12	1.913(7)
Mn1—O14	2.279(7)	W5—O9	1.936(5)
Mn2—O13^{i}	1.911(7)	W5—O6	1.982(7)
Mn2—O13	1.911(7)	W5—O11	2.314(7)
Mn2—O22	1.959(8)	W5—Mn2	3.213(2)
Mn2—O22^{i}	1.959(8)	K1—O16^{ii}	2.763(7)
Mn2—O23	2.133(11)	K1—O23	2.802(13)
Mn2—O11	2.266(10)	K1—O4^{iv}	2.849(10)
W1—O4	1.703(10)	K1—O25	2.932(12)
W1—O1	1.872(7)	K1—O22	3.107(8)
W1—O3	1.957(7)	K1—O21	3.363(12)
W1—O2	2.326(9)	K2—O17	2.818(8)
W2—O16	1.707(7)	K2—O5	2.879(7)
W2—O15	1.858(7)	K2—O1	2.962(7)
W2—O17	1.922(7)	K2—O3	2.987(7)
W2—O12	1.922(7)	K3—O26	2.658(13)
W2—O5	1.987(7)	K3—O8^{vi}	2.827(8)
W2—O14	2.300(7)	K3—O10^{ii}	2.841(7)
W3—O20	1.710(7)	K3—O20^{vii}	2.842(10)
W3—O18	1.827(7)	K3—O18	2.845(8)
W3—O19	1.899(2)	K3—O24	2.891(8)
W3—O17	1.964(7)	K3—O26^{vii}	2.935(18)
W3—O1	1.976(7)	Si1—O14	1.615(7)
W3—O14	2.347(7)	Si1—O11	1.618(10)
W4—O8	1.716(7)	Si1—O2	1.638(9)
W4—O6	1.877(7)	Mn1—Mn2^{i}	3.583(3)
W4—O5	1.881(7)	Mn2—Mn1	3.583(3)
W4—O7	1.942(5)	Mn1—Mn1^{i}	3.537(2)

Table S2. Selected angles

O1—W1—O2	85.82(21)	O16^{II}—K1—O16^{III}	147.18(18)
O1—W1—O1^{I}	88.7(4)	O16^{II}—K1—O23	76.24(17)
O1—W1—O3^{I}	157.9(3)	O16^{II}—K1—O4^{IV}	77.39(16)
O1—W1—O3	88.4(3)	O23—K1—O4^{IV}	72.02(31)
O1^{I}—W1—O3	157.9(3)	O16^{II}—K1—O25	72.30(31)
O3—W1—O2	72.21(20)	O16^{III}—K1—O25	135.79(31)
O3^{I}—W1—O3	86.2(4)	O23—K1—O25	147.78(27)
O4—W1—O2	168.0(4)	O4^{IV}—K1—O25	107.04(27)
O4—W1—O3	99.3(3)	O25^{I}—K1—O25	64.30(38)
O4—W1—O1	102.7(3)	O23—K1—O22^{I}	59.11(15)
O15—W2—O17	91.5(3)	O4^{IV}—K1—O22^{I}	122.54(13)
O16—W2—O17	97.8(3)	O25^{I}—K1—O22^{I}	99.88(31)
O16—W2—O15	101.3(3)	O25—K1—O22^{I}	130.39(31)
O16—W2—O12	100.7(3)	O16^{II}—K1—O22	63.89(21)
O15—W2—O12	93.2(3)	O16^{III}—K1—O22	114.76(20)
O17—W2—O12	159.6(39)	O23—K1—O22	59.11(15)
O16—W2—O5	98.8(3)	O4^{IV}—K1—O22	122.54(13)
O15—W2—O5	159.9(3)	O25^{I}—K1—O22	130.39(31)
O17—W2—O5	85.4(3)	O25—K1—O22	99.88(31)
O12—W2—O5	83.5(3)	O22^{I}—K1—O22	53.18(20)
O16—W2—O14	172.5(3)	O16^{II}—K1—O21	100.74(16)
O15—W2—O14	77.5(3)	O23—K1—O21	98.64(31)
O17—W2—O14	74.9(3)	O4^{IV}—K1—O21	170.65(29)
O12—W2—O14	86.7(3)	O25—K1—O21	80.78(27)
O5—W2—O14	82.5(3)	O22^{I}—K1—O21	49.70(13)
O16—W2—Mn1	133.7(3)	O22—K1—O21	49.70(13)
O15—W2—Mn1	32.6(3)	O17—K2—O5^{V}	124.57(20)
O17—W2—Mn1	83.5(22)	O17—K2—O5	55.43(20)
O12—W2—Mn1	89.8(2)	O5^{V}—K2—O5	179.99(19)
O5—W2—Mn1	127.3(2)	O17—K2—O1^{V}	125.57(20)
O14—W2—Mn1	44.97(16)	O5—K2—O1^{V}	115.21(18)
O20—W3—O18	102.7(3)	O17—K2—O1	54.43(20)
O20—W3—O19	102.2(4)	O5^{V}—K2—O1	115.21(18)

O18—W3—O19	93.3(4)	O5—K2—O1	64.79(18)
O20—W3—O17	98.1(3)	O1^{v}—K2—O1	180.00(19)
O18—W3—O17	91.1(3)	O17—K2—O3^{v}	87.46(20)
O19—W3—O17	157.7(4)	O5—K2—O3^{v}	126.07(18)
O20—W3—O1	99.8(3)	O1—K2—O3^{v}	126.62(17)
O18—W3—O1	157.5(3)	O17—K2—O3	92.54(20)
O19—W3—O1	83.2(4)	O5—K2—O3	53.93(18)
O17—W3—O1	84.4(3)	O1—K2—O3	53.38(17)
O20—W3—O14	171.1(3)	O3^{v}—K2—O3	179.99(18)
O18—W3—O14	76.3(3)	O26—K3—O8^{vi}	91.70(37)
O19—W3—O14	86.7(4)	O26—K3—O10^{ii}	159.00(38)
O17—W3—O14	73.1(3)	O8^{vi}—K3—O10^{ii}	68.02(24)
O1—W3—O14	81.3(3)	O26—K3—O20^{vii}	86.66(37)
O8—W4—O6	102.0(3)	O8^{vi}—K3—O20^{vii}	74.64(23)
O8—W4—O5	102.2(3)	O10^{ii}—K3—O20^{vii}	82.77(23)
O6—W4—O5	88.1(3)	O26—K3—O18	71.57(37)
O8—W4—O7	98.7(4)	O8^{vi}—K3—O18	124.40(27)
O6—W4—O7	89.3(4)	O10^{ii}—K3—O18	123.91(26)
O5—W4—O7	159.0(3)	O20^{vii}—K3—O18	150.40(25)
O8—W4—O3	98.5(3)	O26—K3—O24	119.60(37)
O6—W4—O3	159.5(3)	O8^{vi}—K3—O24	86.78(25)
O5—W4—O3	88.1(3)	O10^{ii}—K3—O24	66.65(21)
O7—W4—O3	87.1(4)	O20^{vii}—K3—O24	148.57(24)
O8—W4—O2	168.3(3)	O18—K3—O24	60.75(23)
O6—W4—O2	86.9(3)	O26—K3—O26^{vii}	82.69(45)
O5—W4—O2	85.4(3)	O8^{vi}—K3—O26^{vii}	136.39(36)
O7—W4—O2	73.6(3)	O10^{ii}—K3—O26^{vii}	107.84(35)
O3—W4—O2	72.7(3)	O20^{vii}—K3—O26^{vii}	61.91(33)
O10—W5—O13	100.4(3)	O18—K3—O26^{vii}	94.78(34)
O10—W5—O12	101.0(3)	O24—K3—O26^{vii}	133.21(35)
O13—W5—O12	90.7(3)	O14—Si1—O14^{i}	109.82(32)
O10—W5—O9	98.4(4)	O14—Si1—O11	110.80(24)
O13—W5—O9	91.7(4)	O14—Si1—O2	108.78(27)
O12—W5—O9	159.7(4)	O11—Si1—O2	107.79(52)

O10—W5—O6	100.5(3)	W1—O1—W3	149.77(43)
O13—W5—O6	159.0(3)	W1—O1—K2	106.09(25)
O12—W5—O6	84.3(3)	W3—O1—K2	102.63(29)
O9—W5—O6	86.3(4)	Si1—O2—W4	122.80(1)
O10—W5—O11	172.7(3)	$W4^{I}$—O2—W4	93.10(1)
O13—W5—O11	76.7(3)	Si1—O2—W1	122.04(50)
O12—W5—O11	85.8(3)	W4—O2—W1	94.11(1)
O9—W5—O11	75.1(3)	W4—O3—W1	120.90(35)
O6—W5—O11	82.6(3)	W4—O3—K2	100.66(26)
O10—W5—Mn2	132.0(3)	W1—O3—K2	102.82(24)
O13—W5—Mn2	31.9(2)	W1—O4—$K1^{VIII}$	179.95(50)
O12—W5—Mn2	88.3(2)	W4—O5—W2	150.12(43)
O9—W5—Mn2	83.1(3)	W4—O5—K2	106.23(28)
O6—W5—Mn2	127.4(2)	W2—O5—K2	102.02(27)
O11—W5—Mn2	44.80(1)	W4—O6—W5	149.09(40)
O21—Mn1—O22	90.34(24)	$W4^{I}$—O7—W4	119.65(1)
O21—Mn1—O15	173.37(21)	W4—O8—$K3^{IX}$	160.20(41)
O22—Mn1—O15	89.45(31)	$W5^{I}$—O9—W5	117.56(1)
O21—Mn1—O18	92.28(20)	W5—O10—$K3^{II}$	122.55(35)
O22—Mn1—O18	170.55(30)	Si1—O11—Mn2	121.30(51)
O15—Mn1—O18	86.89(28)	Si1—O11—W5	127.24(1)
O21—Mn1—O24	93.84(22)	Mn2—O11—W5	89.11(1)
O22—Mn1—O24	98.49(31)	$W5^{I}$—O11—W5	91.31(1)
O15—Mn1—O24	92.74(32)	W5—O12—W2	153.22(40)
O18—Mn1—O24	90.39(30)	W5—O13—Mn2	117.40(42)
O21—Mn1—O14	96.82(18)	Si1—O14—Mn1	122.10(39)
O22—Mn1—O14	94.80(29)	Si1—O14—W2	126.42(34)
O15—Mn1—O14	76.60(29)	Mn1—O14—W2	89.52(26)
O18—Mn1—O14	75.88(28)	Si1—O14—W3	126.58(37)
O24—Mn1—O14	162.89(31)	Mn1—O14—W3	89.05(24)
O21—Mn1—W2	142.31(6)	W2—O14—W3	92.04(24)
O22—Mn1—W2	91.46(24)	W2—O15—Mn1	116.32(38)
O15—Mn1—W2	31.08(21)	W2—O16—$K1^{II}$	167.50(34)
O18—Mn1—W2	80.93(22)	W2—O17—W3	118.81(35)

O24—Mn1—W2	123.02(25)	W2—O17—K2	106.01(28)
O14—Mn1—W2	45.52(20)	W3—O17—K2	107.96(30)
O13^{i}—Mn2—O13	88.79(33)	W3—O18—Mn1	118.80(36)
O13—Mn2—O22	89.90(33)	W3—O18—K3	131.09(37)
O13—Mn2—O22^{i}	172.65(33)	Mn1—O18—K3	107.63(30)
O22—Mn2—O22^{i}	90.47(32)	W3^{i}—O19—W3	154.69(1)
O13—Mn2—O23	96.16(22)	W3—O20—K3^{vii}	153.94(37)
O22—Mn2—O23	91.17(21)	Mn1^{i}—O21—Mn1	134.92(5)
O13—Mn2—O11	76.84(23)	Mn1—O21—K1	93.55(4)
O22—Mn2—O11	95.82(22)	Mn1—O22—Mn2	134.14(40)
O23—Mn2—O11	170.06(40)	Mn1—O22—K1	101.43(27)
O13—Mn2—W5^{i}	82.04(24)	Mn2—O22—K1	89.24(28)
O22—Mn2—W5^{i}	141.91(23)	Mn2—O23—K1	94.45(44)
O13—Mn2—W5	30.76(24)	Mn1—O24—K3	100.58(30)
O22—Mn2—W5	93.17(24)	K3—O26—K3^{vii}	97.31(47)
O23—Mn2—W5	126.60(1)	Mn1^{i}—Mn1—Mn2^{i}	60.42(3)
O11—Mn2—W5	46.09(1)	Mn1^{i}—Mn2—Mn1	59.16(3)
W5^{i}—Mn2—W5	62.02(1)		

Symmetry codes:

(i) x, 0.5-y, z; (ii) 1-x, -y, 1-z; (iii) 1-x, 0.5+y, 1-z; (iv) -1+x, y, -1+z; (v) 2-x, -y, 2-z; (vi) -1+x, y, z; (vii) 1-x, -y, 2-z; (viii) 1+x, y, 1+z; (ix) 1+x, y, z; (x) 1+x, 0.5-y, z; (xi) 1-x, -0.5+y, 1-z; (xii) 1-x, 0.5+y, 2-z; (xiii) 2-x, 0.5+y, 2-z; (xiv) x, y, 1+z.

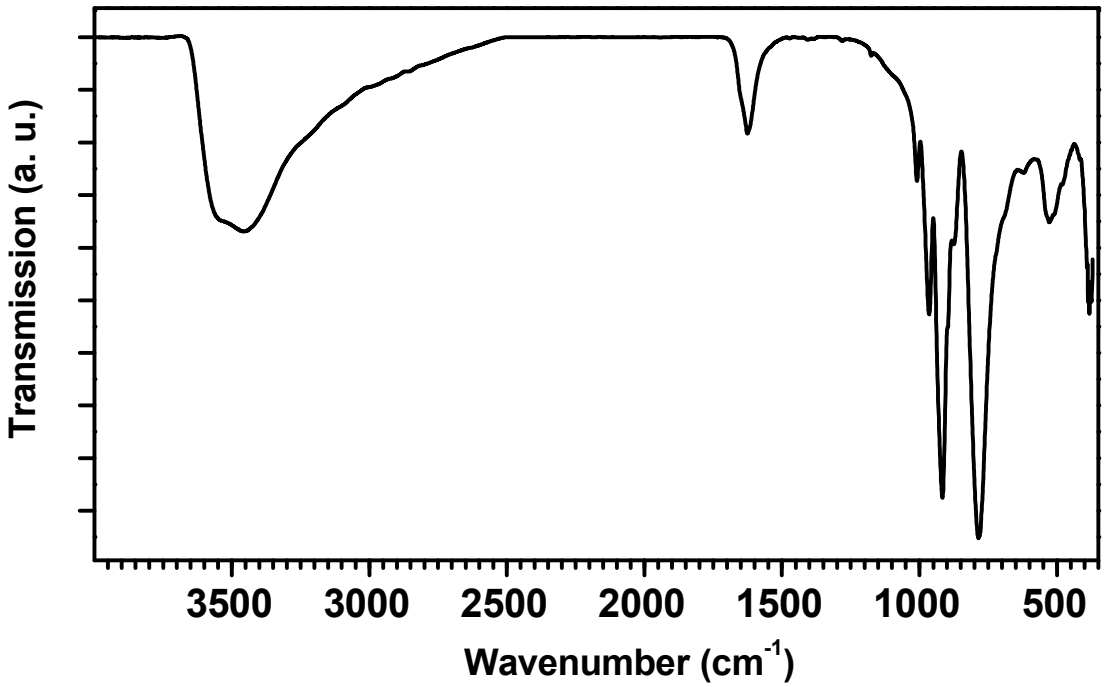


Figure S4. IR spectrum of **1**.

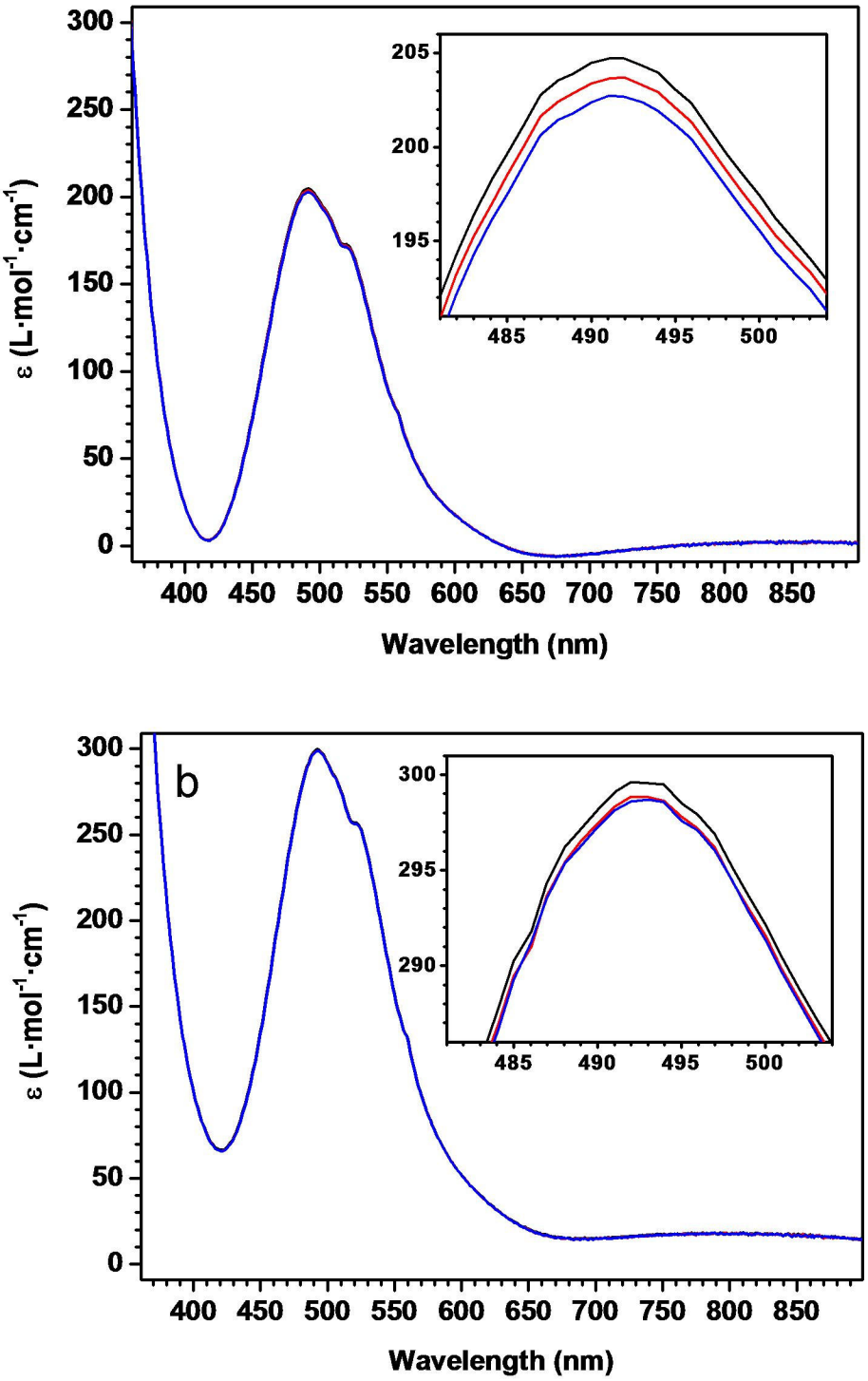


Figure S5. Stability of **1** in aqueous solution. A) UV-visible spectra of an 1 mM solution of **1** in 100 mM Lutidine.HClO4 buffer (pH 7.0). B) UV-visible spectra of an 1 mM solution of **1** in H2O. The spectra were measured directly (black), 30 min (red), and 60 min (blue) after dissolution. Inset: a zoom-in of the molar extinction coefficient (ε) in the 480-505 nm range.

The solution was filtered before the measurement.

Table S3. Assignment of the groups of peaks in the ESI mass spectrum.

experimental m/z	Species (calculated m/z)
1294.9	$[M]H_2 \cdot 5H_2O^{2-}$ (1295.15)
1313.9	$[M]KH \cdot 5H_2O^{2-}$ (1314.12)
1350.7	$[M]K_2 \cdot 7H_2O^{2-}$ (1350.61)
1367.5	$[M]KH \cdot 11H_2O^{2-}$ (1367.66)
1386.5	$[M]K_2 \cdot 11H_2O^{2-}$ (1386.63)
1405.7	$[Mn^{III}_3(OH)_4(H_2O)_2SiW_9O_{34}]K_3 \cdot 11H_2O^{2-}$ (1405.61)

[M] = $[Mn^{III}_3(OH)_3(H_2O)_3SiW_9O_{34}]$;

Table S4. Assignment of the groups of peaks in the MALDI TOF mass spectrum.

experimental m/z	Species (calculated m/z)	
2683.5	$\{[M]KH_2(H_2O)_8\}^-$ (2682.28)	$\{[M]K_2H(H_2O)_6\}^-$ (2684.22)
2702.6	$\{[M]KH_2(H_2O)_9\}^-$ (2700.29)	$\{[M]K_2H(H_2O)_7\}^-$ (2702.29)
2721.4	$\{[M]KH_2(H_2O)_{10}\}^-$ (2718.30)	$\{[M]K_2H(H_2O)_8\}^-$ (2720.24) $\{[M]K_3(H_2O)_6\}^-$ (2722.17)
2737.4	$\{[M]KH_2(H_2O)_{11}\}^-$ (2736.31)	$\{[M]K_2H(H_2O)_9\}^-$ (2738.25)
2817.3	$\{[M]KH_2(H_2O)_7(DHAP)\}^-$ (2816.32)	$\{[M]K_2H(H_2O)_5(DHAP)\}^-$ (2818.25)
2835.3	$\{[M]KH_2(H_2O)_8(DHAP)\}^-$ (2834.33)	$\{[M]K_2H(H_2O)_6(DHAP)\}^-$ (2836.26)
2853.3	$\{[M]KH_2(H_2O)_9(DHAP)\}^-$ (2852.34)	$\{[M]K_2H(H_2O)_7(DHAP)\}^-$ (2854.27)
2872.1	$\{[M]KH_2(H_2O)_{10}(DHAP)\}^-$ (2871.36)	$\{[M]K_2H(H_2O)_8(DHAP)\}^-$ (2873.29)
2890.1	$\{[M]KH_2(H_2O)_{11}(DHAP)\}^-$ (2888.36)	$\{[M]K_2H(H_2O)_9(DHAP)\}^-$ (2890.29) $\{[M]K_3(H_2O)_7(DHAP)\}^-$ (2892.23)
2969.2	$\{[Mn]KH_2(H_2O)_8(DHAP)_2\}^-$ (2968.36)	$\{[Mn]K_2H(H_2O)_6(DHAP)_2\}^-$ (2970.30)

[M] = $[Mn^{III}_3(OH)_3(H_2O)_3SiW_9O_{34}]$; DHPA = 2,5-dihydroxyacetophenone

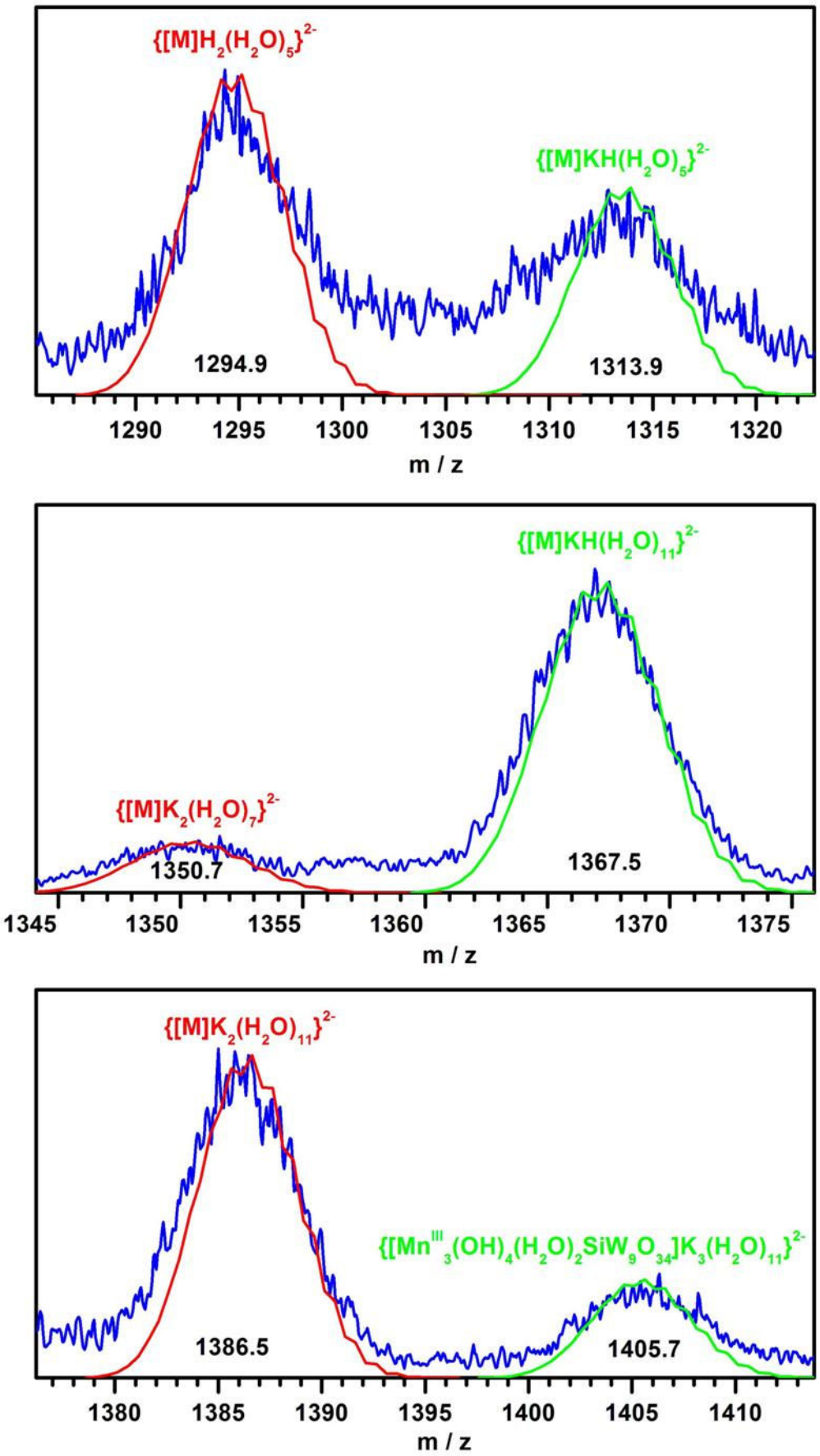


Fig. S6. Isotopic distributions for the species found in the ESI mass spectrum. The blue is the actual spectrum, the red and green lines show the predicted envelopes. [M] = $[Mn^{III}_3(OH)_3(H_2O)_3SiW_9O_{34}]$.

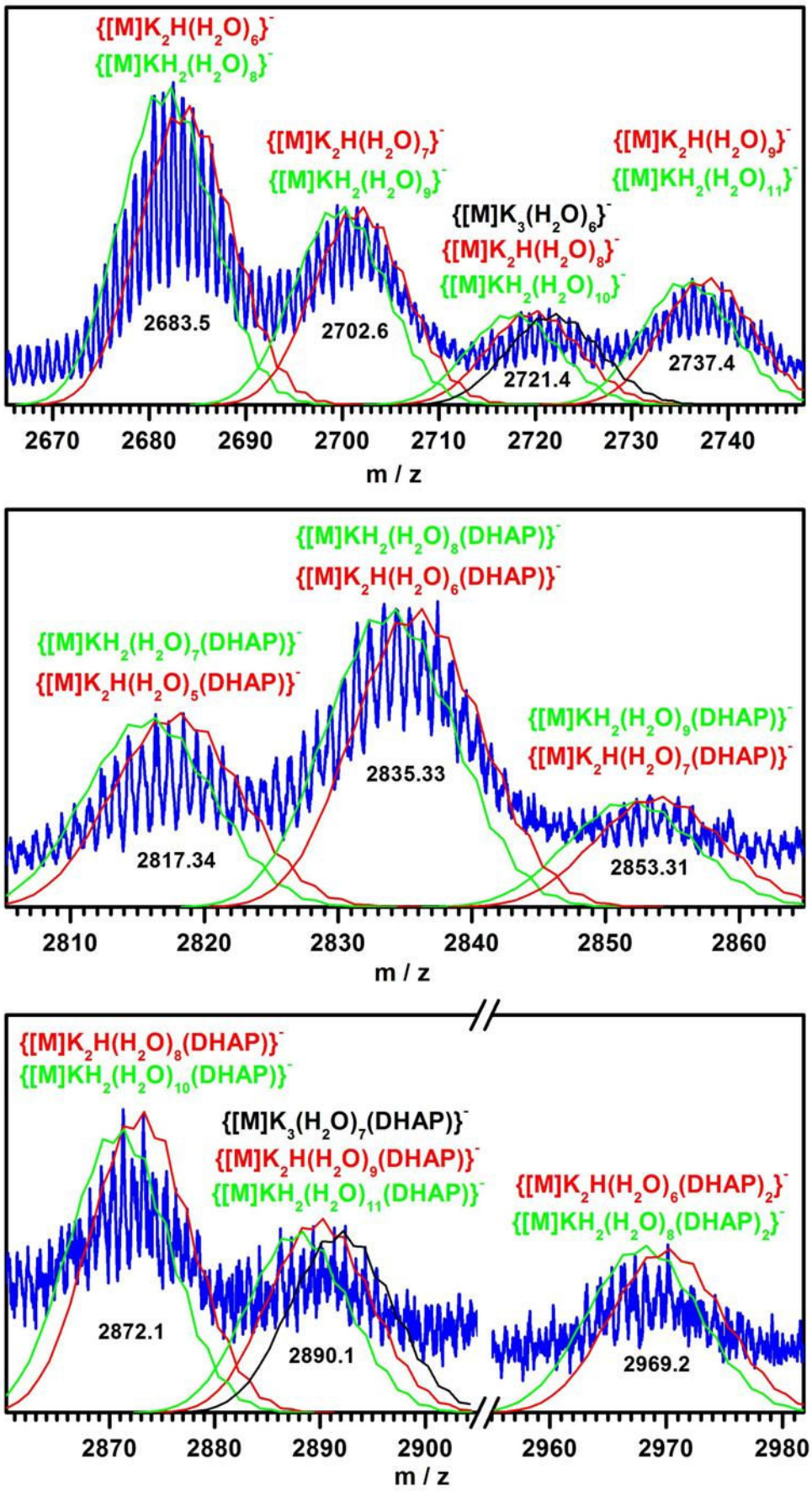


Fig. S7. Isotopic distributions for the species found in the MALDI TOF mass spectrum of **1**. The blue is the actual spectrum, the red, green and black lines show the predicted envelopes from single species. [M] = $[Mn^{III}_3(OH)_3(H_2O)_3SiW_9O_{34}]$; DHPA = 2,5-dihydroxyacetophenone