

Supporting Information

Synthesis, crystal structures and magnetic properties of a family of manganese phosphonate clusters with diverse structures

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Table S1. Selected bond lengths (Å) and angles (deg) for cluster 2

Mn(1)–O(1) #2	1.860(3)	Mn(2)–O(5) #3	1.861(4)
Mn(1)–O(1)	1.860(3)	Mn(2)–O(5) #4	1.861(4)
Mn(1)–O(3)	1.871(3)	Mn(2)–O(5) #5	1.861(4)
Mn(1)–O(3) #3	1.871(3)	Mn(2)–O(5)	1.861(4)
Mn(1)–O(2)	2.181(5)	Mn(2)–O(4)	2.201(7)
O(1)-Mn(1)-O(1)#2	90.5(3)	O(5)-Mn(2)-O(5)#3	177.4(2)
O(1)-Mn(1)-O(3)#2	89.5(2)	O(5)-Mn(2)-O(5)#4	89.970(6)
O(1)#2-Mn(1)-O(3)#2	177.17(17)	O(5)#3-Mn(2)-O(5)#4	89.970(6)
O(1)-Mn(1)-O(3)	177.17(17)	O(5)-Mn(2)-O(5)#5	89.970(6)
O(1)#2-Mn(1)-O(3)	89.5(2)	O(5)#3-Mn(2)-O(5)#5	89.970(6)
O(3)#2-Mn(1)-O(3)	90.4(3)	O(5)#4-Mn(2)-O(5)#5	177.4(2)
O(1)-Mn(1)-O(2)	90.72(15)	O(5)-Mn(2)-O(4)	91.30(12)
O(1)#2-Mn(1)-O(2)	90.72(15)	O(5)#3-Mn(2)-O(4)	91.30(12)
O(3)#2-Mn(1)-O(2)	92.11(15)	O(5)#4-Mn(2)-O(4)	91.30(12)
O(3)-Mn(1)-O(2)	92.11(15)	O(5)#5-Mn(2)-O(4)	91.30(12)

Symmetry transformations used to generate equivalent atoms: #1 -y+1,x+1,-z #2 x,y,-z #3 y-1,-x+1,z
#4 -y+1,x+1,z #5 -x,-y+2,z #6 y-1,-x+1,-z

Table S2. Selected bond lengths (Å) and angles (deg) for cluster 3

O(1)-Mn(1)	1.910(3)	O(35)-Mn(9)	2.223(4)
O(2)-Mn(2)	1.913(3)	O(35)-Mn(13)	2.253(3)

O(3)-Mn(7)	1.891(3)	O(36)-Mn(10)	1.925(3)
O(4)-Mn(1)	2.228(3)	O(36)-Mn(9)	1.932(3)
O(4)-Mn(2)	2.242(3)	O(37)-Mn(11)	1.923(3)
O(5)-Mn(6)	1.874(4)	O(37)-Mn(9)	1.961(3)
O(6)-Mn(2)	1.939(3)	O(37)-Mn(8)	2.000(3)
O(6)-Mn(1)	1.953(3)	O(37)-Mn(10)	2.286(3)
O(6)-Mn(3)	1.953(3)	O(38)-Mn(11)	1.918(3)
O(7)-Mn(2)	1.947(3)	O(38)-Mn(13)#2	1.973(3)
O(7)-Mn(4)	1.950(3)	O(38)-Mn(8)	1.975(3)
O(7)-Mn(3)	1.954(3)	O(39)-Mn(11)	2.208(3)
O(8)-Mn(2)	1.913(3)	O(39)-Mn(9)	2.241(4)
O(9)-Mn(4)	2.234(3)	O(40)-Mn(9)	1.895(3)
O(9)-Mn(2)	2.263(3)	O(40)-Mn(13)	1.925(3)
O(10)-Mn(6)	1.899(4)	O(40)-Mn(8)	2.279(3)
O(11)-Mn(6)	1.873(4)	O(40)-Mn(14)	2.316(3)
O(12)-Mn(6)	2.239(5)	O(41)-Mn(9)	1.934(3)
O(13)-Mn(1)#1	2.227(4)	O(42)-Mn(13)	1.916(3)
O(13)-Mn(4)	2.231(3)	O(43)-Mn(13)	1.904(4)
O(14)-Mn(4)	1.911(4)	O(44)-Mn(14)	1.940(4)
O(14)-Mn(5)	2.017(4)	O(45)-Mn(14)	2.411(5)
O(15)-Mn(4)	1.916(3)	O(46)-Mn(14)	1.943(4)
O(15)-Mn(1)#1	1.937(3)	O(46)-Mn(12)	1.954(4)
O(15)-Mn(5)	1.941(3)	O(47)-Mn(14)	1.871(4)
O(15)-Mn(3)	2.444(3)	O(48)-Mn(12)	1.869(4)
O(16)-Mn(5)	2.006(4)	O(50)-Mn(12)	1.900(4)
O(17)-Mn(5)	1.930(4)	O(52)-Mn(4)	1.919(3)
O(20)-Mn(5)	2.115(4)	O(53)-Mn(12)	2.205(5)
O(21)-Mn(7)#1	1.874(4)	Mn(1)-O(15)#1	1.937(3)
O(22)-Mn(7)	1.874(4)	Mn(1)-O(13)#1	2.227(4)
O(23)-Mn(7)	1.922(4)	Mn(3)-O(7)#1	1.954(3)
O(23)-Mn(6)#1	1.929(4)	Mn(3)-O(6)#1	1.953(3)
O(24)-Mn(7)	2.220(5)	Mn(3)-O(15)#1	2.444(3)
O(25)-Mn(1)	1.900(4)	Mn(5)-O(25)#1	2.072(4)
O(25)-Mn(5)#1	2.072(4)	Mn(6)-O(23)#1	1.929(4)

O(28)-Mn(10)	1.934(4)	Mn(7)-O(21)#1	1.874(4)
O(29)-Mn(14)#2	1.880(4)	Mn(8)-O(38)#2	1.975(3)
O(30)-Mn(11)	2.202(3)	Mn(8)-O(37)#2	2.000(3)
O(30)-Mn(13)#2	2.234(3)	Mn(8)-O(40)#2	2.279(3)
O(31)-Mn(10)	1.925(4)	Mn(12)-O(34)#2	1.856(4)
O(31)-Mn(11)	1.952(4)	Mn(13)-O(38)#2	1.973(3)
O(32)-Mn(10)	2.160(4)	Mn(13)-O(30)#2	2.234(3)
O(33)-Mn(10)	1.897(4)	Mn(14)-O(29)#2	1.880(4)
O(34)-Mn(12)#2	1.856(4)	O(14)-Mn(4)-O(9)	91.89(15)
O(25)-Mn(1)-O(15)#1	83.78(16)	O(15)-Mn(4)-O(9)	85.17(13)
O(1)-Mn(1)-O(15)#1	178.87(15)	O(52)-Mn(4)-O(9)	93.69(14)
O(25)-Mn(1)-O(6)	169.29(16)	O(7)-Mn(4)-O(9)	82.86(12)
O(1)-Mn(1)-O(6)	93.94(14)	O(13)-Mn(4)-O(9)	167.16(13)
O(15)#1-Mn(1)-O(6)	86.76(13)	O(17)-Mn(5)-O(15)	170.06(17)
O(25)-Mn(1)-O(4)	91.97(16)	O(17)-Mn(5)-O(16)	94.03(17)
O(1)-Mn(1)-O(4)	94.25(14)	O(15)-Mn(5)-O(16)	92.34(15)
O(15)#1-Mn(1)-O(4)	84.96(13)	O(17)-Mn(5)-O(14)	94.46(16)
O(6)-Mn(1)-O(4)	82.21(13)	O(15)-Mn(5)-O(14)	79.37(14)
O(25)-Mn(1)-O(13)#1	90.10(16)	O(16)-Mn(5)-O(14)	171.45(15)
O(1)-Mn(1)-O(13)#1	98.76(14)	O(17)-Mn(5)-O(25)#1	93.22(16)
O(15)#1-Mn(1)-O(13)#1	82.08(13)	O(15)-Mn(5)-O(25)#1	79.30(14)
O(6)-Mn(1)-O(13)#1	93.55(13)	O(16)-Mn(5)-O(25)#1	88.76(17)
O(4)-Mn(1)-O(13)#1	166.58(13)	O(14)-Mn(5)-O(25)#1	91.76(16)
O(8)-Mn(2)-O(2)	88.48(15)	O(17)-Mn(5)-O(20)	92.69(15)
O(8)-Mn(2)-O(6)	177.21(14)	O(15)-Mn(5)-O(20)	94.73(13)
O(2)-Mn(2)-O(6)	94.23(14)	O(16)-Mn(5)-O(20)	91.72(16)
O(8)-Mn(2)-O(7)	93.81(14)	O(14)-Mn(5)-O(20)	86.89(15)
O(2)-Mn(2)-O(7)	177.50(14)	O(25)#1-Mn(5)-O(20)	174.03(14)
O(6)-Mn(2)-O(7)	83.48(13)	O(37)#2-Mn(8)-O(40)#2	74.99(12)
O(8)-Mn(2)-O(4)	98.60(14)	O(40)-Mn(8)-O(40)#2	180.0(2)
O(2)-Mn(2)-O(4)	88.46(14)	O(11)-Mn(6)-O(5)	175.37(18)
O(6)-Mn(2)-O(4)	82.13(13)	O(11)-Mn(6)-O(10)	88.77(16)
O(7)-Mn(2)-O(4)	90.23(13)	O(5)-Mn(6)-O(10)	93.56(17)
O(8)-Mn(2)-O(9)	89.47(14)	O(11)-Mn(6)-O(23)#1	90.80(16)

O(2)-Mn(2)-O(9)	98.83(14)	O(5)-Mn(6)-O(23)#1	87.31(17)
O(6)-Mn(2)-O(9)	89.48(13)	O(10)-Mn(6)-O(23)#1	173.89(17)
O(7)-Mn(2)-O(9)	82.18(12)	O(11)-Mn(6)-O(12)	88.38(18)
O(4)-Mn(2)-O(9)	169.30(12)	O(5)-Mn(6)-O(12)	87.56(18)
O(7)#1-Mn(3)-O(7)	180.0	O(10)-Mn(6)-O(12)	91.56(19)
O(7)#1-Mn(3)-O(6)#1	82.92(12)	O(23)#1-Mn(6)-O(12)	94.5(2)
O(7)-Mn(3)-O(6)#1	97.08(12)	O(21)#1-Mn(7)-O(22)	175.75(18)
O(7)#1-Mn(3)-O(6)	97.08(12)	O(21)#1-Mn(7)-O(3)	88.77(15)
O(7)-Mn(3)-O(6)	82.92(12)	O(22)-Mn(7)-O(3)	92.95(16)
O(6)#1-Mn(3)-O(6)	180.000(1)	O(21)#1-Mn(7)-O(23)	90.43(15)
O(7)#1-Mn(3)-O(15)#1	73.86(12)	O(22)-Mn(7)-O(23)	88.28(16)
O(7)-Mn(3)-O(15)#1	106.14(12)	O(3)-Mn(7)-O(23)	173.71(17)
O(6)#1-Mn(3)-O(15)#1	106.10(12)	O(21)#1-Mn(7)-O(24)	88.23(18)
O(6)-Mn(3)-O(15)#1	73.90(12)	O(22)-Mn(7)-O(24)	87.82(18)
O(7)#1-Mn(3)-O(15)	106.14(12)	O(3)-Mn(7)-O(24)	92.39(18)
O(7)-Mn(3)-O(15)	73.86(12)	O(23)-Mn(7)-O(24)	93.83(19)
O(6)#1-Mn(3)-O(15)	73.90(12)	O(38)-Mn(8)-O(38)#2	180.0(3)
O(6)-Mn(3)-O(15)	106.10(12)	O(38)-Mn(8)-O(37)	79.55(13)
O(15)#1-Mn(3)-O(15)	180.000(1)	O(38)#2-Mn(8)-O(37)	100.45(13)
O(14)-Mn(4)-O(15)	82.69(15)	O(38)-Mn(8)-O(37)#2	100.45(13)
O(14)-Mn(4)-O(52)	96.29(15)	O(38)#2-Mn(8)-O(37)#2	79.55(13)
O(15)-Mn(4)-O(52)	178.44(15)	O(37)-Mn(8)-O(37)#2	180.00(19)
O(14)-Mn(4)-O(7)	169.16(15)	O(38)-Mn(8)-O(40)	101.54(12)
O(15)-Mn(4)-O(7)	87.41(13)	O(38)#2-Mn(8)-O(40)	78.46(12)
O(52)-Mn(4)-O(7)	93.51(14)	O(37)-Mn(8)-O(40)	74.99(12)
O(14)-Mn(4)-O(13)	89.82(15)	O(37)#2-Mn(8)-O(40)	105.01(12)
O(15)-Mn(4)-O(13)	82.43(13)	O(38)-Mn(8)-O(40)#2	78.46(12)
O(52)-Mn(4)-O(13)	98.77(14)	O(38)#2-Mn(8)-O(40)#2	101.54(12)
O(7)-Mn(4)-O(13)	93.26(13)	O(37)-Mn(8)-O(40)#2	105.01(12)
O(40)-Mn(9)-O(36)	170.62(14)	O(37)#2-Mn(8)-O(40)#2	74.99(12)
O(40)-Mn(9)-O(41)	91.01(14)	O(40)-Mn(8)-O(40)#2	180.0(2)
O(36)-Mn(9)-O(41)	97.44(15)	O(51)-Mn(11)-O(38)	94.56(15)
O(40)-Mn(9)-O(37)	85.35(13)	O(51)-Mn(11)-O(37)	177.40(16)
O(36)-Mn(9)-O(37)	85.92(14)	O(38)-Mn(11)-O(37)	82.92(14)

O(41)-Mn(9)-O(37)	174.44(15)	O(51)-Mn(11)-O(31)	94.94(16)
O(40)-Mn(9)-O(35)	87.29(13)	O(38)-Mn(11)-O(31)	166.80(16)
O(36)-Mn(9)-O(35)	88.52(16)	O(37)-Mn(11)-O(31)	87.65(15)
O(41)-Mn(9)-O(35)	90.72(15)	O(51)-Mn(11)-O(30)	91.25(15)
O(37)-Mn(9)-O(35)	84.93(13)	O(38)-Mn(11)-O(30)	84.52(13)
O(40)-Mn(9)-O(39)	95.74(14)	O(37)-Mn(11)-O(30)	89.19(13)
O(36)-Mn(9)-O(39)	86.28(16)	O(31)-Mn(11)-O(30)	86.13(14)
O(41)-Mn(9)-O(39)	103.60(15)	O(51)-Mn(11)-O(39)	97.13(15)
O(37)-Mn(9)-O(39)	80.98(13)	O(38)-Mn(11)-O(39)	99.44(14)
O(35)-Mn(9)-O(39)	165.28(13)	O(37)-Mn(11)-O(39)	82.66(13)
O(33)-Mn(10)-O(31)	172.28(17)	O(31)-Mn(11)-O(39)	88.45(15)
O(33)-Mn(10)-O(36)	90.46(18)	O(30)-Mn(11)-O(39)	170.39(14)
O(31)-Mn(10)-O(36)	89.13(17)	O(34)#2-Mn(12)-O(53)	85.6(2)
O(33)-Mn(10)-O(28)	90.48(18)	O(48)-Mn(12)-O(53)	87.9(2)
O(31)-Mn(10)-O(28)	88.49(17)	O(50)-Mn(12)-O(53)	91.9(2)
O(36)-Mn(10)-O(28)	169.14(15)	O(46)-Mn(12)-O(53)	96.6(2)
O(33)-Mn(10)-O(32)	93.10(19)	O(43)-Mn(13)-O(42)	89.35(15)
O(31)-Mn(10)-O(32)	94.60(18)	O(43)-Mn(13)-O(40)	175.66(16)
O(36)-Mn(10)-O(32)	97.59(16)	O(42)-Mn(13)-O(40)	91.10(15)
O(28)-Mn(10)-O(32)	93.16(16)	O(43)-Mn(13)-O(38)#2	92.27(14)
O(33)-Mn(10)-O(37)	93.72(15)	O(42)-Mn(13)-O(38)#2	174.20(15)
O(31)-Mn(10)-O(37)	78.67(14)	O(40)-Mn(13)-O(38)#2	87.70(13)
O(36)-Mn(10)-O(37)	77.58(13)	O(43)-Mn(13)-O(30)#2	89.50(15)
O(28)-Mn(10)-O(37)	91.57(13)	O(42)-Mn(13)-O(30)#2	103.18(14)
O(32)-Mn(10)-O(37)	171.67(16)	O(40)-Mn(13)-O(30)#2	86.20(13)
O(34)#2-Mn(12)-O(48)	173.43(19)	O(38)#2-Mn(13)-O(30)#2	82.41(12)
O(34)#2-Mn(12)-O(50)	92.09(19)	O(43)-Mn(13)-O(35)	98.60(15)
O(48)-Mn(12)-O(50)	88.90(18)	O(42)-Mn(13)-O(35)	89.14(14)
O(34)#2-Mn(12)-O(46)	89.26(18)	O(40)-Mn(13)-O(35)	85.72(14)
O(48)-Mn(12)-O(46)	90.72(17)	O(38)#2-Mn(13)-O(35)	85.11(13)
O(50)-Mn(12)-O(46)	171.49(17)	O(30)#2-Mn(13)-O(35)	165.38(12)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table S3. Selected Bond Lengths (Å) and Angles (deg) for Cluster 4

K(1)-O(13)	2.714(8)	Mn(3)-O(4)	1.937(4)
K(1)-O(18)	2.731(5)	Mn(3)-O(20)	2.182(4)
K(1)-O(12)	2.739(11)	Mn(3)-O(8)	2.186(5)
K(1)-O(26)	2.821(5)	Mn(3)-Mn(7)	2.9131(16)
K(1)-O(21)	2.842(5)	Mn(3)-Mn(6)	3.1077(16)
K(1)-O(12')	2.85(3)	Mn(3)-Mn(4)	3.1642(18)
K(1)-O(33)	2.86(6)	Mn(3)-Mn(1)#1	3.18(2)
K(1)-Mn(5)	3.458(2)	Mn(4)-O(2)#1	1.856(4)
Mn(1)-O(1)	2.18(2)	Mn(4)-O(23)#1	1.928(4)
Mn(1)-O(3)#1	2.23(2)	Mn(4)-O(16)	1.931(4)
Mn(1)-O(1)#1	2.30(2)	Mn(4)-O(1)	2.001(4)
Mn(1)-O(4)#1	2.31(2)	Mn(4)-O(29)	2.198(5)
Mn(1)-O(3)	2.33(2)	Mn(4)-O(8)	2.341(5)
Mn(1)-O(4)	2.511(19)	Mn(5)-O(2)	1.857(4)
Mn(1)-Mn(3)#1	3.18(2)	Mn(5)-O(21)	1.940(4)
Mn(1)-Mn(6)	3.19(2)	Mn(5)-O(26)	1.946(4)
Mn(1)-Mn(6)#1	3.20(2)	Mn(5)-O(3)	1.967(4)
Mn(2)-O(11)	1.872(5)	Mn(5)-O(18)	2.159(5)
Mn(2)-O(3)	1.928(4)	Mn(5)-O(7)#1	2.443(6)
Mn(2)-O(25)	1.933(4)	Mn(6)-O(15)	1.894(4)
Mn(2)-O(4)#1	1.956(4)	Mn(6)-O(24)	1.896(4)
Mn(2)-O(28)	2.205(4)	Mn(6)-O(1)	1.949(4)
Mn(2)-O(7)#1	2.224(5)	Mn(6)-O(3)	1.951(4)
Mn(2)-Mn(7)#1	2.9422(15)	Mn(6)-O(20)	2.242(4)
Mn(2)-Mn(6)	3.1087(15)	Mn(6)-O(28)	2.247(4)
Mn(2)-Mn(5)	3.1378(18)	Mn(6)-Mn(1)#1	3.20(2)
Mn(3)-O(6)	1.883(4)	Mn(7)-O(10)	1.901(5)
Mn(3)-O(17)	1.911(5)	Mn(7)-O(4)	1.967(4)
Mn(3)-O(1)	1.918(4)	Mn(7)-O(6)	1.972(4)
Mn(3)-O(4)	1.937(4)	Mn(7)-O(27)#1	1.979(5)
Mn(3)-O(20)	2.182(4)	Mn(7)-O(11)#1	2.082(5)
Mn(3)-O(8)	2.186(5)	Mn(7)-O(19)	2.107(5)
Mn(2)-O(7)#1	2.224(5)	Mn(7)-Mn(2)#1	2.9422(15)
Mn(2)-Mn(7)#1	2.9422(15)	Mn(8)-O(22)	2.154(5)
Mn(2)-Mn(6)	3.1087(15)	Mn(8)-O(5)	2.160(5)
Mn(2)-Mn(5)	3.1378(18)	Mn(8)-O(19)	2.213(5)
Mn(3)-O(6)	1.883(4)	Mn(8)-O(2)	2.215(4)
Mn(3)-O(17)	1.911(5)	Mn(8)-O(27)#1	2.366(5)
Mn(3)-O(1)	1.918(4)	Mn(8)-O(29)#1	2.446(6)
O(13)-K(1)-O(18)	82.98(19)	O(23)#1-Mn(4)-O(1)	163.54(19)
O(13)-K(1)-O(12)	99.7(3)	O(16)-Mn(4)-O(1)	91.20(17)
O(18)-K(1)-O(12)	141.4(3)	O(2)#1-Mn(4)-O(29)	85.0(2)
O(13)-K(1)-O(26)	137.25(18)	O(23)#1-Mn(4)-O(29)	91.24(19)

O(18)-K(1)-O(26)	61.23(14)	O(16)-Mn(4)-O(29)	91.9(2)
O(12)-K(1)-O(26)	122.7(3)	O(1)-Mn(4)-O(29)	105.15(18)
O(13)-K(1)-O(21)	87.04(19)	O(2)#1-Mn(4)-O(8)	99.49(19)
O(18)-K(1)-O(21)	63.47(13)	O(23)#1-Mn(4)-O(8)	85.92(19)
O(12)-K(1)-O(21)	154.6(4)	O(16)-Mn(4)-O(8)	83.7(2)
O(26)-K(1)-O(21)	57.35(13)	O(1)-Mn(4)-O(8)	77.85(17)
O(13)-K(1)-O(12')	85.2(8)	O(29)-Mn(4)-O(8)	174.8(2)
O(18)-K(1)-O(12')	125.1(8)	O(2)-Mn(5)-O(21)	92.93(18)
O(12)-K(1)-O(12')	20.6(7)	O(2)-Mn(5)-O(26)	174.4(2)
O(26)-K(1)-O(12')	133.6(7)	O(21)-Mn(5)-O(26)	88.73(19)
O(21)-K(1)-O(12')	167.4(6)	O(2)-Mn(5)-O(3)	87.81(17)
O(13)-K(1)-O(33)	115.8(11)	O(21)-Mn(5)-O(3)	163.20(18)
O(18)-K(1)-O(33)	160.5(11)	O(26)-Mn(5)-O(3)	92.16(18)
O(12)-K(1)-O(33)	45.0(12)	O(2)-Mn(5)-O(18)	87.64(19)
O(26)-K(1)-O(33)	99.5(11)	O(21)-Mn(5)-O(18)	91.22(18)
O(21)-K(1)-O(33)	110.1(12)	O(26)-Mn(5)-O(18)	86.93(19)
O(12')-K(1)-O(33)	64.9(14)	O(3)-Mn(5)-O(18)	105.58(17)
O(1)-Mn(1)-O(3)#1	108.9(9)	O(2)-Mn(5)-O(7)#1	102.46(19)
O(1)-Mn(1)-O(3)#1	108.9(9)	O(21)-Mn(5)-O(7)#1	83.65(18)
O(1)-Mn(1)-O(1)#1	170.3(6)	O(26)-Mn(5)-O(7)#1	83.07(19)
O(1)-Mn(1)-O(4)#1	113.0(8)	O(3)-Mn(5)-O(7)#1	79.81(17)
O(3)#1-Mn(1)-O(4)#1	114.3(8)	O(18)-Mn(5)-O(7)#1	168.85(18)
O(1)#1-Mn(1)-O(4)#1	72.9(6)	O(15)-Mn(6)-O(24)	89.69(19)
O(1)-Mn(1)-O(3)	74.1(7)	O(15)-Mn(6)-O(1)	90.78(18)
O(3)#1-Mn(1)-O(3)	170.4(6)	O(24)-Mn(6)-O(1)	178.52(18)
O(1)#1-Mn(1)-O(3)	101.6(8)	O(15)-Mn(6)-O(3)	179.10(19)
O(4)#1-Mn(1)-O(3)	71.6(6)	O(24)-Mn(6)-O(3)	91.13(18)
O(1)-Mn(1)-O(4)	71.0(6)	O(1)-Mn(6)-O(3)	88.41(17)
O(3)#1-Mn(1)-O(4)	69.6(6)	O(15)-Mn(6)-O(20)	94.54(18)
O(1)#1-Mn(1)-O(4)	102.2(6)	O(24)-Mn(6)-O(20)	100.42(17)
O(4)#1-Mn(1)-O(4)	171.9(7)	O(1)-Mn(6)-O(20)	78.15(15)
O(3)-Mn(1)-O(4)	103.7(6)	O(3)-Mn(6)-O(20)	85.67(16)
O(11)-Mn(2)-O(3)	172.11(19)	O(15)-Mn(6)-O(28)	100.62(18)
O(11)-Mn(2)-O(25)	94.2(2)	O(24)-Mn(6)-O(28)	94.97(18)
O(3)-Mn(2)-O(25)	93.68(18)	O(1)-Mn(6)-O(28)	86.32(16)
O(11)-Mn(2)-O(4)#1	83.51(19)	O(3)-Mn(6)-O(28)	78.94(16)
O(3)-Mn(2)-O(4)#1	88.60(17)	O(20)-Mn(6)-O(28)	158.41(16)
O(25)-Mn(2)-O(4)#1	176.23(18)	O(10)-Mn(7)-O(4)	164.6(2)
O(11)-Mn(2)-O(28)	99.7(2)	O(10)-Mn(7)-O(6)	90.9(2)
O(3)-Mn(2)-O(28)	80.47(16)	O(4)-Mn(7)-O(6)	78.94(17)
O(25)-Mn(2)-O(28)	87.36(18)	O(10)-Mn(7)-O(27)#1	96.3(2)
O(4)#1-Mn(2)-O(28)	90.07(16)	O(4)-Mn(7)-O(27)#1	94.87(17)
O(11)-Mn(2)-O(7)#1	94.7(2)	O(6)-Mn(7)-O(27)#1	171.3(2)

O(3)-Mn(2)-O(7)#1	86.50(19)	O(10)-Mn(7)-O(11)#1	91.1(2)
O(25)-Mn(2)-O(7)#1	82.69(19)	O(4)-Mn(7)-O(11)#1	78.03(18)
O(4)#1-Mn(2)-O(7)#1	100.46(18)	O(6)-Mn(7)-O(11)#1	93.1(2)
O(28)-Mn(2)-O(7)#1	163.05(18)	O(27)#1-Mn(7)-O(11)#1	91.6(2)
O(6)-Mn(3)-O(17)	94.04(19)	O(22)-Mn(8)-O(5)	86.0(2)
O(6)-Mn(3)-O(1)	171.95(18)	O(22)-Mn(8)-O(19)	139.22(18)
O(17)-Mn(3)-O(1)	93.56(18)	O(5)-Mn(8)-O(19)	86.2(2)
O(6)-Mn(3)-O(4)	81.90(18)	O(22)-Mn(8)-O(2)	90.13(17)
O(17)-Mn(3)-O(4)	175.92(18)	O(5)-Mn(8)-O(2)	175.5(2)
O(1)-Mn(3)-O(4)	90.48(16)	O(19)-Mn(8)-O(2)	98.24(16)
O(6)-Mn(3)-O(20)	97.4(2)	O(22)-Mn(8)-O(27)#1	145.51(18)
O(17)-Mn(3)-O(20)	87.47(19)	O(5)-Mn(8)-O(27)#1	81.24(19)
O(1)-Mn(3)-O(20)	80.33(16)	O(19)-Mn(8)-O(27)#1	71.85(17)
O(4)-Mn(3)-O(20)	92.62(16)	O(2)-Mn(8)-O(27)#1	100.79(16)
O(6)-Mn(3)-O(8)	100.0(2)	O(22)-Mn(8)-O(29)#1	92.43(18)
O(17)-Mn(3)-O(8)	83.1(2)	O(5)-Mn(8)-O(29)#1	105.7(2)
O(1)-Mn(3)-O(8)	83.55(18)	O(19)-Mn(8)-O(29)#1	128.17(18)
O(4)-Mn(3)-O(8)	97.93(19)	O(2)-Mn(8)-O(29)#1	72.13(16)
O(20)-Mn(3)-O(8)	160.79(18)	O(27)#1-Mn(8)-O(29)#1	61.02(17)
O(2)#1-Mn(4)-O(23)#1	91.87(19)	O(23)#1-Mn(4)-O(16)	89.76(19)
O(2)#1-Mn(4)-O(16)	176.5(2)	O(2)#1-Mn(4)-O(1)	88.12(17)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table S4. Bond-valence sums for the Mn and O^a atoms of cluster 3

Atom	BVS	Assigned oxidation state	Atom	BVS	Group
Mn1	2.38	+2	O3	1.95	<i>t</i> -BuPO ₃ ²⁻
Mn2	2.82	+3	O6	1.88	<i>t</i> -BuPO ₃ ²⁻
Mn3	2.90	+3	O7	1.97	<i>t</i> -BuPO ₃ ²⁻
Mn4	2.93	+3	O8	2.01	<i>t</i> -BuPO ₃ ²⁻
Mn5	2.75	+3	O9	1.91	<i>t</i> -BuPO ₃ ²⁻
Mn6	2.91	+3	O10	1.90	<i>t</i> -BuPO ₃ ²⁻
			O11	1.91	<i>t</i> -BuPO ₃ ²⁻
			O12	1.85	<i>t</i> -BuPO ₃ ²⁻
			O13	1.97	<i>t</i> -BuPO ₃ ²⁻
			O14	1.60	<i>t</i> -BuPO ₃ ²⁻
			O15	2.05	<i>t</i> -BuPO ₃ ²⁻
			O16	1.88	<i>t</i> -BuPO ₃ ²⁻
			O17	1.85	<i>t</i> -BuPO ₃ ²⁻

	O18	1.86	<i>t</i> -BuPO ₃ ²⁻
	O19	1.99	<i>t</i> -BuPO ₃ ²⁻
	O21	1.1	CH ₃ CH ₃ CHO ⁻
	O22	0.18	H ₂ O
	O23	0.42	CH ₃ OH
	O24	0.24	H ₂ O

^a BVS values for O atoms of RO⁻, ROH and H₂O groups are typically 1.8–2.0, 1.0–1.2 and 0–0.2, respectively, but can be affected by hydrogen bonding.

Table S5 Bond-valence sums for the Mn and O^a atoms of cluster 4

Atom	BVS	Assigned oxidation state	Atom	BVS	Group
Mn1	1.64	+2	O5	0.34	H ₂ O
Mn2	3.12	+3	O6	2.22	CH ₃ O ⁻
Mn3	3.22	+3	O7	1.94	C ₆ H ₅ COO ⁻
Mn4	3.02	+3	O8	2.01	C ₆ H ₅ COO ⁻
Mn5	3.03	+3	O9	1.61	C ₆ H ₅ COO ⁻
Mn6	3.05	+3	O10	2.02	C ₆ H ₅ COO ⁻
Mn7	3.11	+3	O11	2.15	CH ₃ O ⁻
Mn8	1.86	+2	O12	0.02	H ₂ O
			O13	0.03	H ₂ O
			O14	0.04	H ₂ O
			O15	1.95	<i>t</i> -BuPO ₃ ²⁻
			O16	1.89	<i>t</i> -BuPO ₃ ²⁻
			O17	1.93	<i>t</i> -BuPO ₃ ²⁻
			O18	1.94	<i>t</i> -BuPO ₃ ²⁻
			O19	1.93	<i>t</i> -BuPO ₃ ²⁻
			O20	1.62	<i>t</i> -BuPO ₃ ²⁻
			O21	1.98	<i>t</i> -BuPO ₃ ²⁻
			O22	1.64	<i>t</i> -BuPO ₃ ²⁻
			O23	1.90	<i>t</i> -BuPO ₃ ²⁻
			O24	1.92	<i>t</i> -BuPO ₃ ²⁻
			O25	1.93	<i>t</i> -BuPO ₃ ²⁻
			O26	2.00	<i>t</i> -BuPO ₃ ²⁻

O27	1.97	<i>t</i> -BuPO ₃ ²⁻
O28	1.87	<i>t</i> -BuPO ₃ ²⁻
O29	1.76	<i>t</i> -BuPO ₃ ²⁻
O33	0.04	H ₂ O

^a BVS values for O atoms of RO⁻, ROH and H₂O groups are typically 1.8–2.0, 1.0–1.2 and 0–0.2, respectively, but can be affected by hydrogen bonding.

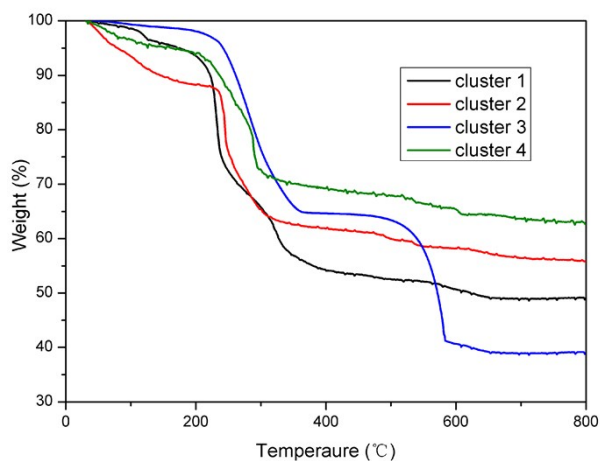


Figure S1. The TGA of cluster 1-4

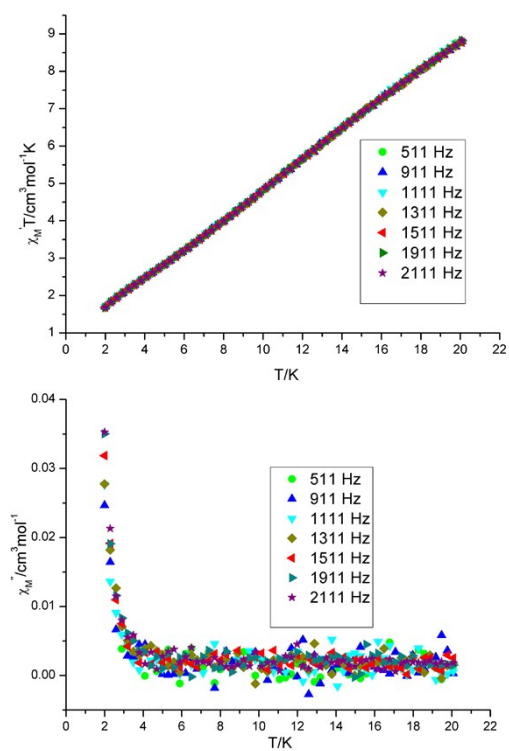


Figure S2. Ac susceptibility in-phase $\chi' / M T$ (top) and out-of-phase χ'' / M (bottom) signals of cluster 1 in a 3.0 G field oscillating at the indicated frequencies

