

A Functionalized Polyoxometalate Solid for Selective Oxidation of Styrene to Benzaldehyde

Jing Tang,^{1,2} Xiu-Li Yang,¹ Xian-Wei Zhang,¹ Miao Wang¹ and Chuan-De Wu^{1*}

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Department of Chemistry and Chemical Engineering, Heihe University, Heihe 164300, P. R. China

Figures

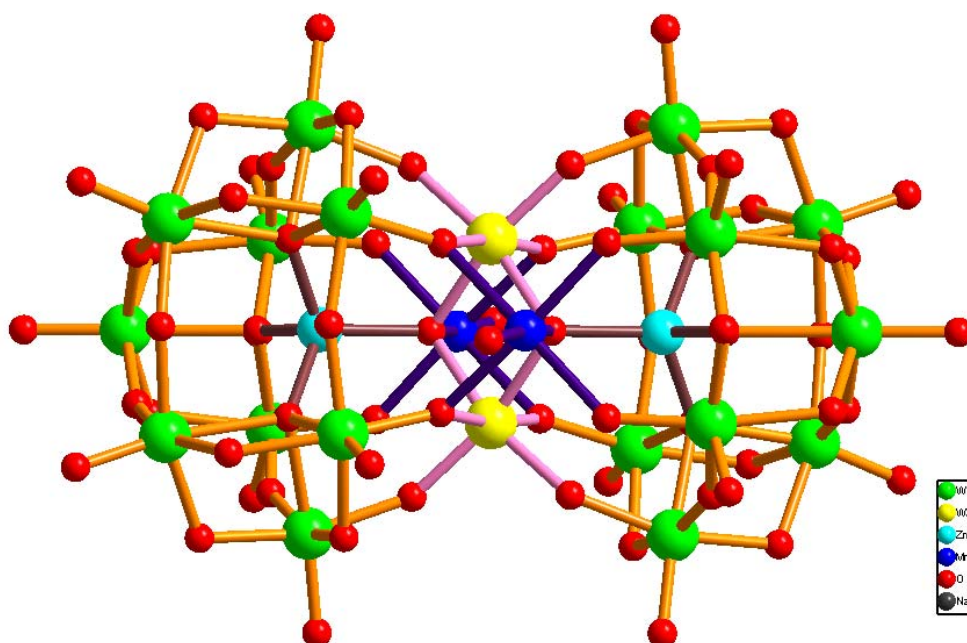


Figure S1. Ball-and-stick representation of the polyanion $\{\text{Mn}_2\text{Zn}_3\text{W}_{19}\}$ in $[\text{Na}_{12}(\text{H}_2\text{O})_{38}][\text{WZn}\{\text{Mn}(\text{H}_2\text{O})\}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 3\text{H}_2\text{O}$.

* E-mail address: cdwu@zju.edu.cn

¹ Zhejiang University

² Heihe University

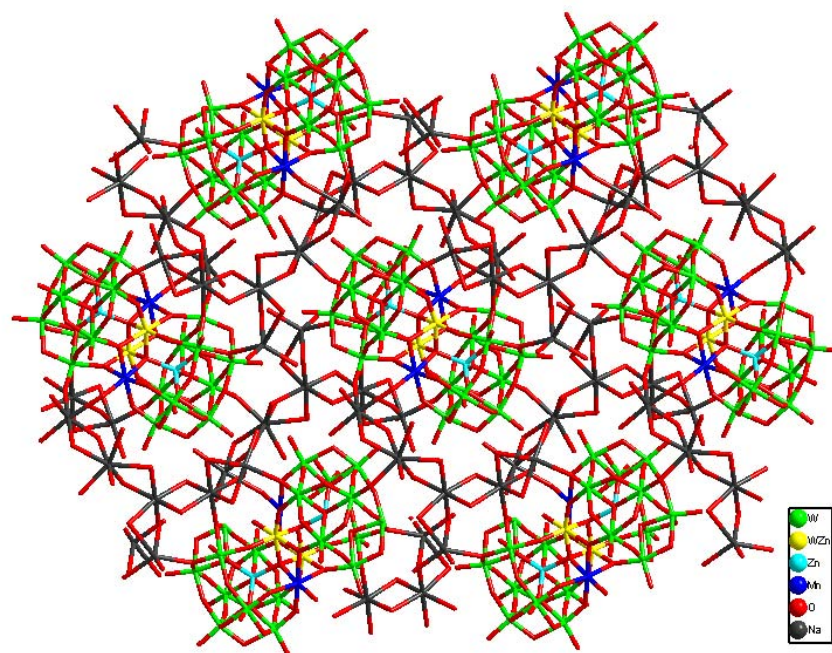


Figure S2. A view of the lamellar network of the polyanion $\{\text{Mn}_2\text{Zn}_3\text{W}_{19}\}$ linked by sodium ions in $[\text{Na}_{12}(\text{H}_2\text{O})_{38}][\text{WZn}\{\text{Mn}(\text{H}_2\text{O})\}_2(\text{ZnW}_9\text{O}_{34})_2]\cdot 3\text{H}_2\text{O}$.

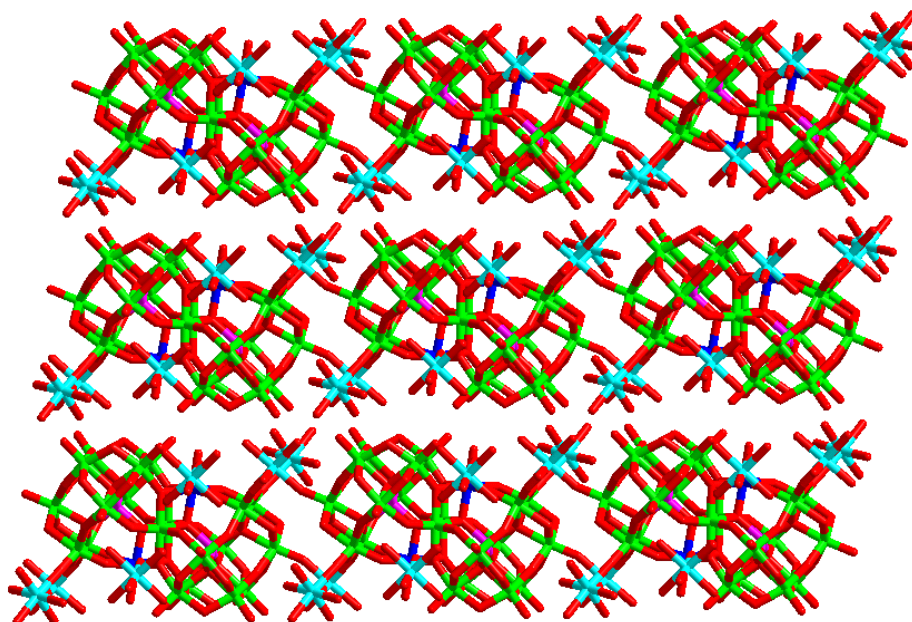


Figure S3. Packing diagram of **1** viewed down the *b* axis.

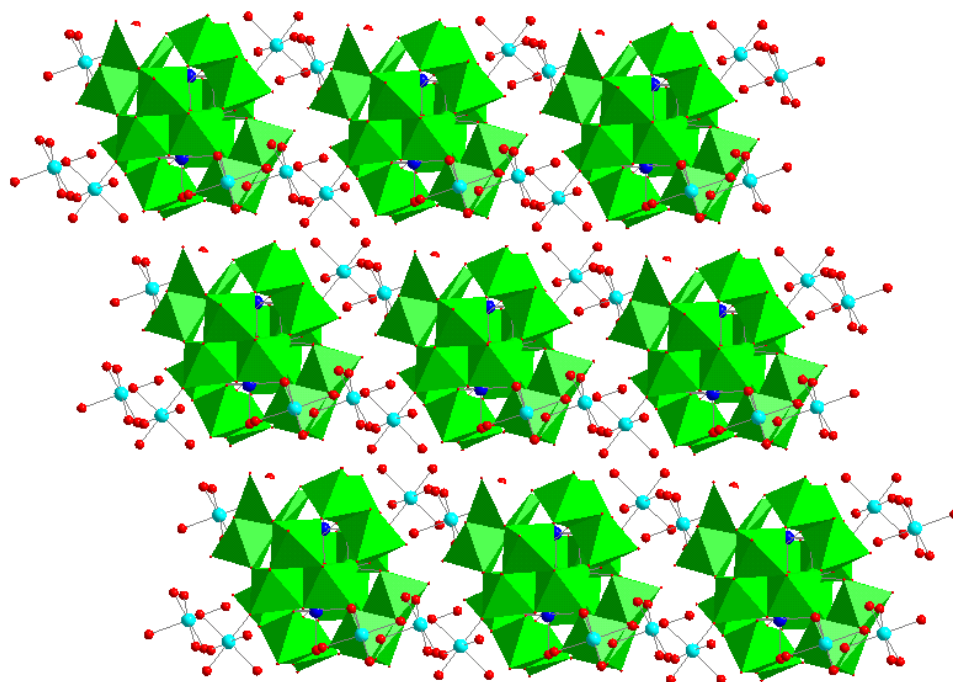


Figure S4. Packing diagram of **1** viewed down the *c* axis.

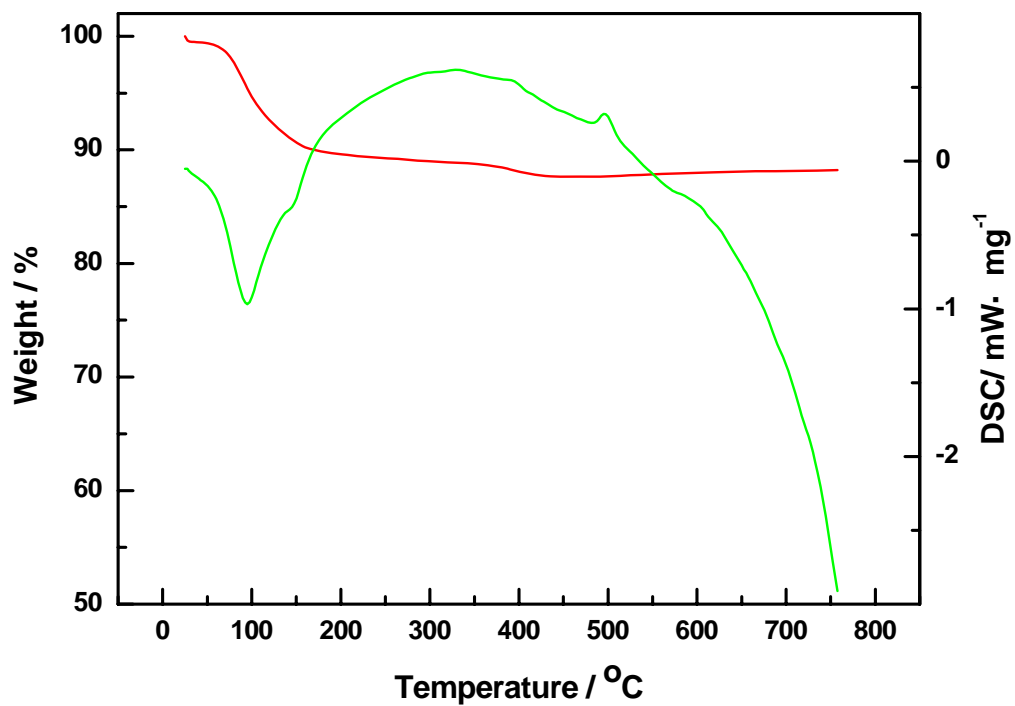


Figure S5. Thermogravimetric analysis result of **1**.

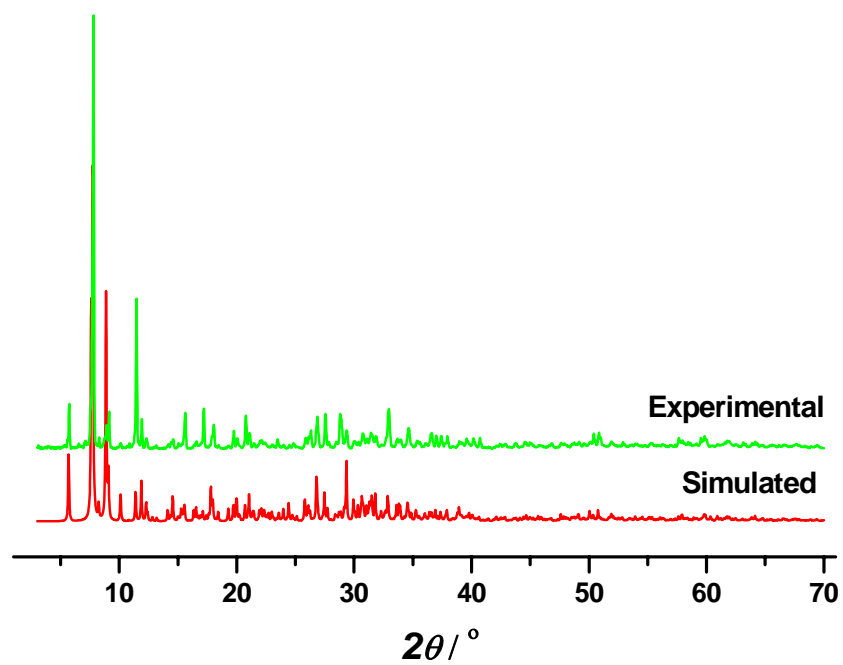


Figure S6. Powder X-ray diffraction patterns for compound **1**.

Tables

Table S1. Selected bond lengths (Å) for **1**.

Bond lengths	(Å)	Bond lengths	(Å)	Bond lengths	(Å)
W(1)-O(28)	1.735(9)	W(6)-O(9)	1.969(9)	Co(1)-O(5)	2.056(8)
W(1)-O(12)	1.840(9)	W(6)-O(44)	1.983(9)	Co(1)-O(21)	2.065(10)
W(1)-O(26)	1.910(10)	W(6)-O(35)	2.184(10)	Co(1)-O(3)	2.102(10)
W(1)-O(10)	1.968(9)	W(7)-O(27)	1.730(10)	Co(1)-O(8)#1	2.154(10)
W(1)-O(9)	1.978(10)	W(7)-O(16)	1.901(9)	Co(1)-O(16)#1	2.174(9)
W(1)-O(35)	2.163(9)	W(7)-O(4)	1.933(11)	Co(2)-O(25)	2.022(9)
W(2)-O(47)	1.695(11)	W(7)-O(46)	1.952(10)	Co(2)-O(32)#2	2.056(9)
W(2)-O(6)	1.902(10)	W(7)-O(14)	1.957(9)	Co(2)-O(49)	2.071(10)
W(2)-O(7)	1.902(9)	W(7)-O(34)	2.155(9)	Co(2)-O(22)	2.124(12)
W(2)-O(46)	1.973(9)	W(8)-O(48)	1.728(10)	Co(2)-O(19)	2.130(10)
W(2)-O(30)	1.978(8)	W(8)-O(8)	1.906(9)	Co(2)-O(24)	2.134(11)
W(2)-O(34)	2.197(9)	W(8)-O(44)	1.915(11)	Co(3)-O(29)	2.055(10)
W(3)-O(25)	1.756(9)	W(8)-O(4)	1.931(11)	Co(3)-O(42)	2.085(11)
W(3)-O(11)	1.834(10)	W(8)-O(10)	1.937(9)	Co(3)-O(43)	2.095(11)
W(3)-O(15)	1.840(9)	W(8)-O(35)	2.188(8)	Co(3)-O(37)	2.107(13)
W(3)-O(12)	1.994(9)	W(9)-O(29)	1.725(10)	Co(3)-O(36)	2.133(12)
W(3)-O(13)	1.998(9)	W(9)-O(3)	1.764(9)	Co(3)-O(38)	2.141(12)
W(3)-O(33)	2.209(9)	W(9)-O(17)	1.926(9)	Co(4)-O(50)	2.070(10)
W(4)-O(32)	1.729(9)	W(9)-O(31)	1.990(9)	Co(4)-O(45)	2.089(11)
W(4)-O(2)	1.794(9)	W(9)-O(11)	2.104(9)	Co(4)-O(39)	2.098(11)
W(4)-O(7)	1.913(9)	W(9)-O(33)	2.138(9)	Co(4)-O(40)	2.120(12)
W(4)-O(31)	1.916(10)	W(10)-O(6)	1.939(11)	Co(4)-O(41)	2.160(10)
W(4)-O(15)	2.090(9)	W(10)-O(1)#1	1.968(12)	Co(4)-O(18)	2.181(11)
W(4)-O(33)	2.149(9)	W(10)-O(5)	2.014(10)	O(1)-Zn(2)#1	1.968(12)
W(4)-W(9)	3.2289(9)	W(10)-O(5)#1	2.017(9)	O(1)-W(10)#1	1.968(12)
W(5)-O(23)	1.743(9)	W(10)-O(16)	2.061(9)	O(5)-Zn(2)#1	2.017(9)
W(5)-O(13)	1.840(9)	W(10)-O(8)#1	2.064(9)	O(5)-W(10)#1	2.017(9)
W(5)-O(30)	1.931(9)	W(10)-Zn(2)#1	3.122(2)	O(8)-Zn(2)#1	2.064(9)
W(5)-O(14)	1.969(9)	W(10)-W(10)#1	3.122(2)	O(8)-W(10)#1	2.064(9)
W(5)-O(26)	1.969(10)	Zn(1)-O(35)	1.900(9)	O(8)-Co(1)#1	2.154(10)
W(5)-O(34)	2.157(9)	Zn(1)-O(5)	1.916(9)	O(16)-Co(1)#1	2.174(9)
W(6)-O(20)	1.689(11)	Zn(1)-O(34)	1.920(10)	O(32)-Co(2)#2	2.056(9)
W(6)-O(17)	1.896(9)	Zn(1)-O(33)	1.928(9)		
W(6)-O(1)	1.909(11)	Co(1)-O(2)	2.049(9)		

Table S2. Selected angles (°) for **1**.

Bond angles	(°)	Bond angles	(°)
O(28)-W(1)-O(12)	101.0(4)	O(1)#1-W(10)-O(5)#1	93.6(4)
O(28)-W(1)-O(26)	99.6(5)	O(5)-W(10)-O(5)#1	78.5(4)
O(12)-W(1)-O(26)	87.3(4)	O(6)-W(10)-O(16)	88.2(4)
O(28)-W(1)-O(10)	97.8(4)	O(1)#1-W(10)-O(16)	95.7(4)
O(12)-W(1)-O(10)	161.2(4)	O(5)-W(10)-O(16)	93.2(4)
O(26)-W(1)-O(10)	88.0(4)	O(5)#1-W(10)-O(16)	82.9(4)
O(28)-W(1)-O(9)	96.2(5)	O(6)-W(10)-O(8)#1	96.2(4)
O(12)-W(1)-O(9)	89.8(4)	O(1)#1-W(10)-O(8)#1	88.1(4)
O(26)-W(1)-O(9)	164.2(4)	O(5)-W(10)-O(8)#1	82.3(4)
O(10)-W(1)-O(9)	89.8(4)	O(5)#1-W(10)-O(8)#1	92.1(4)
O(28)-W(1)-O(35)	168.2(4)	O(16)-W(10)-O(8)#1	173.9(4)
O(12)-W(1)-O(35)	87.5(4)	O(35)-Zn(1)-O(5)	114.0(4)
O(26)-W(1)-O(35)	88.8(4)	O(35)-Zn(1)-O(34)	105.6(4)
O(10)-W(1)-O(35)	74.1(3)	O(5)-Zn(1)-O(34)	113.8(4)
O(9)-W(1)-O(35)	75.5(4)	O(35)-Zn(1)-O(33)	106.6(4)
O(47)-W(2)-O(6)	101.6(5)	O(5)-Zn(1)-O(33)	108.5(4)
O(47)-W(2)-O(7)	104.0(4)	O(34)-Zn(1)-O(33)	107.9(4)
O(6)-W(2)-O(7)	90.7(4)	O(2)-Co(1)-O(5)	92.2(4)
O(47)-W(2)-O(46)	97.2(5)	O(2)-Co(1)-O(21)	89.5(4)
O(6)-W(2)-O(46)	85.4(4)	O(5)-Co(1)-O(21)	178.1(4)
O(7)-W(2)-O(46)	158.8(4)	O(2)-Co(1)-O(3)	88.8(4)
O(47)-W(2)-O(30)	96.4(4)	O(5)-Co(1)-O(3)	93.3(4)
O(6)-W(2)-O(30)	161.0(4)	O(21)-Co(1)-O(3)	87.6(4)
O(7)-W(2)-O(30)	90.8(4)	O(2)-Co(1)-O(8)#1	93.4(4)
O(46)-W(2)-O(30)	86.4(4)	O(5)-Co(1)-O(8)#1	79.2(4)
O(47)-W(2)-O(34)	166.9(4)	O(21)-Co(1)-O(8)#1	99.8(4)
O(6)-W(2)-O(34)	86.7(4)	O(3)-Co(1)-O(8)#1	172.3(4)
O(7)-W(2)-O(34)	85.7(4)	O(2)-Co(1)-O(16)#1	171.4(4)
O(46)-W(2)-O(34)	73.3(4)	O(5)-Co(1)-O(16)#1	79.3(4)
O(30)-W(2)-O(34)	74.5(4)	O(21)-Co(1)-O(16)#1	99.0(4)
O(25)-W(3)-O(11)	99.4(4)	O(3)-Co(1)-O(16)#1	92.5(4)
O(25)-W(3)-O(15)	101.7(4)	O(8)#1-Co(1)-O(16)#1	84.3(4)
O(11)-W(3)-O(15)	97.4(4)	O(25)-Co(2)-O(32)#2	90.8(4)
O(25)-W(3)-O(12)	97.0(4)	O(25)-Co(2)-O(49)	176.2(4)
O(11)-W(3)-O(12)	89.3(4)	O(32)#2-Co(2)-O(49)	86.8(4)
O(15)-W(3)-O(12)	158.9(4)	O(25)-Co(2)-O(22)	90.5(4)
O(25)-W(3)-O(13)	98.6(4)	O(32)#2-Co(2)-O(22)	88.1(4)
O(11)-W(3)-O(13)	160.1(4)	O(49)-Co(2)-O(22)	92.4(4)

O(15)-W(3)-O(13)	87.2(4)	O(25)-Co(2)-O(19)	88.5(4)
O(12)-W(3)-O(13)	80.1(4)	O(32)#2-Co(2)-O(19)	179.1(4)
O(25)-W(3)-O(33)	174.0(4)	O(49)-Co(2)-O(19)	94.0(4)
O(11)-W(3)-O(33)	75.6(4)	O(22)-Co(2)-O(19)	91.4(4)
O(15)-W(3)-O(33)	75.9(4)	O(25)-Co(2)-O(24)	87.3(4)
O(12)-W(3)-O(33)	86.4(3)	O(32)#2-Co(2)-O(24)	92.0(4)
O(13)-W(3)-O(33)	86.8(3)	O(49)-Co(2)-O(24)	89.9(4)
O(32)-W(4)-O(2)	102.6(4)	O(22)-Co(2)-O(24)	177.7(4)
O(32)-W(4)-O(7)	101.5(4)	O(19)-Co(2)-O(24)	88.4(4)
O(2)-W(4)-O(7)	93.9(4)	O(29)-Co(3)-O(42)	175.1(4)
O(32)-W(4)-O(31)	95.7(4)	O(29)-Co(3)-O(43)	86.5(4)
O(2)-W(4)-O(31)	93.1(4)	O(42)-Co(3)-O(43)	89.0(4)
O(7)-W(4)-O(31)	159.6(4)	O(29)-Co(3)-O(37)	92.7(4)
O(32)-W(4)-O(15)	93.2(4)	O(42)-Co(3)-O(37)	89.4(5)
O(2)-W(4)-O(15)	164.0(4)	O(43)-Co(3)-O(37)	92.9(5)
O(7)-W(4)-O(15)	85.0(4)	O(29)-Co(3)-O(36)	95.6(5)
O(31)-W(4)-O(15)	83.0(4)	O(42)-Co(3)-O(36)	88.8(5)
O(32)-W(4)-O(33)	163.2(4)	O(43)-Co(3)-O(36)	176.8(5)
O(2)-W(4)-O(33)	91.5(4)	O(37)-Co(3)-O(36)	89.5(5)
O(7)-W(4)-O(33)	86.4(4)	O(29)-Co(3)-O(38)	90.0(4)
O(31)-W(4)-O(33)	74.2(4)	O(42)-Co(3)-O(38)	87.9(5)
O(15)-W(4)-O(33)	72.5(3)	O(43)-Co(3)-O(38)	87.9(5)
O(23)-W(5)-O(13)	103.2(4)	O(37)-Co(3)-O(38)	177.2(5)
O(23)-W(5)-O(30)	97.3(4)	O(36)-Co(3)-O(38)	89.6(5)
O(13)-W(5)-O(30)	93.2(4)	O(50)-Co(4)-O(45)	88.9(5)
O(23)-W(5)-O(14)	95.3(4)	O(50)-Co(4)-O(39)	92.7(4)
O(13)-W(5)-O(14)	160.6(4)	O(45)-Co(4)-O(39)	92.9(5)
O(30)-W(5)-O(14)	90.0(4)	O(50)-Co(4)-O(40)	178.2(5)
O(23)-W(5)-O(26)	99.0(4)	O(45)-Co(4)-O(40)	89.9(5)
O(13)-W(5)-O(26)	86.3(4)	O(39)-Co(4)-O(40)	88.7(5)
O(30)-W(5)-O(26)	163.4(4)	O(50)-Co(4)-O(41)	90.4(4)
O(14)-W(5)-O(26)	85.3(4)	O(45)-Co(4)-O(41)	84.7(5)
O(23)-W(5)-O(34)	167.0(4)	O(39)-Co(4)-O(41)	176.0(5)
O(13)-W(5)-O(34)	88.6(4)	O(40)-Co(4)-O(41)	88.1(5)
O(30)-W(5)-O(34)	76.3(4)	O(50)-Co(4)-O(18)	87.9(4)
O(14)-W(5)-O(34)	73.6(3)	O(45)-Co(4)-O(18)	175.3(4)
O(26)-W(5)-O(34)	87.1(4)	O(39)-Co(4)-O(18)	90.8(4)
O(20)-W(6)-O(17)	100.9(5)	O(40)-Co(4)-O(18)	93.2(5)
O(20)-W(6)-O(1)	100.8(5)	O(41)-Co(4)-O(18)	91.8(4)
O(17)-W(6)-O(1)	90.0(4)	W(6)-O(1)-Zn(2)#1	143.8(6)
O(20)-W(6)-O(9)	97.3(5)	W(6)-O(1)-W(10)#1	143.8(6)
O(17)-W(6)-O(9)	91.5(4)	Zn(2)#1-O(1)-W(10)#1	0.00(10)
O(1)-W(6)-O(9)	161.3(4)	W(4)-O(2)-Co(1)	138.9(6)
O(20)-W(6)-O(44)	98.3(4)	W(9)-O(3)-Co(1)	137.0(6)

O(17)-W(6)-O(44)	160.8(4)	W(8)-O(4)-W(7)	155.9(5)
O(1)-W(6)-O(44)	85.9(4)	Zn(1)-O(5)-W(10)	115.3(5)
O(9)-W(6)-O(44)	86.7(4)	Zn(1)-O(5)-Zn(2)#1	115.6(5)
O(20)-W(6)-O(35)	169.4(4)	W(10)-O(5)-Zn(2)#1	101.5(4)
O(17)-W(6)-O(35)	86.9(4)	Zn(1)-O(5)-W(10)#1	115.6(5)
O(1)-W(6)-O(35)	86.3(4)	W(10)-O(5)-W(10)#1	101.5(4)
O(9)-W(6)-O(35)	75.2(4)	Zn(2)#1-O(5)-W(10)#1	0.00(5)
O(44)-W(6)-O(35)	74.1(4)	Zn(1)-O(5)-Co(1)	119.8(4)
O(27)-W(7)-O(16)	102.3(5)	W(10)-O(5)-Co(1)	100.9(4)
O(27)-W(7)-O(4)	101.5(4)	Zn(2)#1-O(5)-Co(1)	100.9(4)
O(16)-W(7)-O(4)	88.1(4)	W(10)#1-O(5)-Co(1)	100.9(4)
O(27)-W(7)-O(46)	96.9(5)	W(2)-O(6)-W(10)	143.7(6)
O(16)-W(7)-O(46)	86.5(4)	W(2)-O(7)-W(4)	153.8(5)
O(4)-W(7)-O(46)	161.5(4)	W(8)-O(8)-Zn(2)#1	138.8(5)
O(27)-W(7)-O(14)	96.2(4)	W(8)-O(8)-W(10)#1	138.8(5)
O(16)-W(7)-O(14)	161.3(4)	Zn(2)#1-O(8)-W(10)#1	0.00(7)
O(4)-W(7)-O(14)	91.3(4)	W(8)-O(8)-Co(1)#1	123.6(5)
O(46)-W(7)-O(14)	88.2(4)	Zn(2)#1-O(8)-Co(1)#1	96.1(4)
O(27)-W(7)-O(34)	166.9(4)	W(10)#1-O(8)-Co(1)#1	96.1(4)
O(16)-W(7)-O(34)	87.4(4)	W(6)-O(9)-W(1)	111.7(5)
O(4)-W(7)-O(34)	87.5(4)	W(8)-O(10)-W(1)	114.0(4)
O(46)-W(7)-O(34)	74.6(4)	W(3)-O(11)-W(9)	113.6(5)
O(14)-W(7)-O(34)	73.9(4)	W(1)-O(12)-W(3)	155.7(6)
O(48)-W(8)-O(8)	102.4(5)	W(5)-O(13)-W(3)	156.2(6)
O(48)-W(8)-O(44)	99.4(5)	W(7)-O(14)-W(5)	113.4(4)
O(8)-W(8)-O(44)	90.2(5)	W(3)-O(15)-W(4)	113.5(4)
O(48)-W(8)-O(4)	99.5(5)	W(7)-O(16)-W(10)	139.3(5)
O(8)-W(8)-O(4)	86.1(4)	W(7)-O(16)-Co(1)#1	122.1(4)
O(44)-W(8)-O(4)	161.1(4)	W(10)-O(16)-Co(1)#1	95.7(4)
O(48)-W(8)-O(10)	97.3(4)	W(6)-O(17)-W(9)	153.9(6)
O(8)-W(8)-O(10)	160.3(4)	W(3)-O(25)-Co(2)	160.3(5)
O(44)-W(8)-O(10)	88.1(4)	W(1)-O(26)-W(5)	147.1(5)
O(4)-W(8)-O(10)	89.2(4)	W(9)-O(29)-Co(3)	167.8(6)
O(48)-W(8)-O(35)	169.9(4)	W(5)-O(30)-W(2)	112.4(4)
O(8)-W(8)-O(35)	86.4(4)	W(4)-O(31)-W(9)	111.5(4)
O(44)-W(8)-O(35)	75.3(4)	W(4)-O(32)-Co(2)#2	154.3(6)
O(4)-W(8)-O(35)	85.9(4)	Zn(1)-O(33)-W(9)	118.8(4)
O(10)-W(8)-O(35)	74.1(4)	Zn(1)-O(33)-W(4)	117.4(4)
O(29)-W(9)-O(3)	103.1(5)	W(9)-O(33)-W(4)	97.7(3)
O(29)-W(9)-O(17)	101.4(4)	Zn(1)-O(33)-W(3)	121.6(4)
O(3)-W(9)-O(17)	94.5(4)	W(9)-O(33)-W(3)	98.7(4)
O(29)-W(9)-O(31)	96.8(4)	W(4)-O(33)-W(3)	98.0(3)
O(3)-W(9)-O(31)	93.1(4)	Zn(1)-O(34)-W(7)	118.5(4)
O(17)-W(9)-O(31)	158.2(4)	Zn(1)-O(34)-W(5)	122.8(5)

O(29)-W(9)-O(11)	91.3(4)	W(7)-O(34)-W(5)	99.1(4)
O(3)-W(9)-O(11)	165.4(4)	Zn(1)-O(34)-W(2)	117.0(4)
O(17)-W(9)-O(11)	85.1(4)	W(7)-O(34)-W(2)	98.0(4)
O(31)-W(9)-O(11)	82.5(4)	W(5)-O(34)-W(2)	96.5(4)
O(29)-W(9)-O(33)	161.3(4)	Zn(1)-O(35)-W(1)	122.5(4)
O(3)-W(9)-O(33)	93.3(4)	Zn(1)-O(35)-W(6)	118.1(4)
O(17)-W(9)-O(33)	86.1(4)	W(1)-O(35)-W(6)	97.5(4)
O(31)-W(9)-O(33)	73.0(4)	Zn(1)-O(35)-W(8)	119.2(5)
O(11)-W(9)-O(33)	72.1(4)	W(1)-O(35)-W(8)	97.7(3)
O(6)-W(10)-O(1)#1	95.4(5)	W(6)-O(35)-W(8)	96.5(3)
O(6)-W(10)-O(5)	94.0(4)	W(8)-O(44)-W(6)	113.5(5)
O(1)#1-W(10)-O(5)	167.2(4)	W(7)-O(46)-W(2)	113.6(5)
O(6)-W(10)-O(5)#1	168.0(4)		

Symmetry transformations used to generate equivalent atoms: #1: -x+2, -y+2, -z; #2 : -x+2, -y+2,

-z+1

Table S3. Selected bond lengths (Å) for { $\text{Na}_{12}\text{Mn}_2\text{Zn}_3\text{W}_{19}$ }.

Bond lengths	(Å)	Bond lengths	(Å)	Bond lengths	(Å)
W(1)-O(12)	1.735(11)	W(7)-O(27)	1.772(11)	Na(1)-O(40)	2.395(15)
W(1)-O(17)	1.900(12)	W(7)-O(1)	1.907(11)	Na(1)-O(37)	2.416(14)
W(1)-O(4)	1.920(9)	W(7)-O(11)	1.988(11)	Na(1)-O(51)	2.430(19)
W(1)-O(28)	1.944(9)	W(7)-O(16)	2.107(11)	Na(1)-O(39)	2.476(15)
W(1)-O(9)	1.956(10)	W(7)-O(23)	2.153(10)	Na(1)-Na(3)	3.451(10)
W(1)-O(21)	2.187(9)	W(7)-W(9)	3.2355(9)	Na(1)-Na(6)	3.49(2)
W(2)-O(26)	1.743(10)	W(8)-O(30)	1.732(10)	Na(1)-Na(4)#3	3.722(11)
W(2)-O(25)	1.858(10)	W(8)-O(18)	1.869(10)	Na(2)-O(48)	2.284(17)
W(2)-O(16)	1.872(11)	W(8)-O(22)	1.918(10)	Na(2)-O(41)	2.310(14)
W(2)-O(31)	1.951(9)	W(8)-O(9)	1.972(11)	Na(2)-O(49)	2.347(19)
W(2)-O(18)	1.967(10)	W(8)-O(7)	1.994(10)	Na(2)-O(43)	2.469(15)
W(2)-O(23)	2.237(9)	W(8)-O(21)	2.176(8)	Na(2)-Na(4)	3.858(11)
W(3)-O(2)	1.725(11)	W(8)-Na(6)	3.708(17)	Na(3)-O(38)	2.357(15)
W(3)-O(1)	1.905(11)	W(9)-O(6)	1.729(13)	Na(3)-O(39)	2.376(15)
W(3)-O(5)#1	1.928(9)	W(9)-O(13)	1.780(11)	Na(3)-O(45)	2.396(15)
W(3)-O(20)	1.953(11)	W(9)-O(11)	1.921(11)	Na(3)-O(42)	2.442(13)
W(3)-O(29)	1.982(10)	W(9)-O(32)	1.961(10)	Na(3)-O(37)	2.446(15)
W(3)-O(24)	2.166(9)	W(9)-O(25)	2.095(10)	Na(3)-Na(5)	3.222(10)
W(4)-O(10)	1.727(10)	W(9)-O(23)	2.138(10)	Na(4)-O(44)	2.357(16)
W(4)-O(32)	1.871(10)	W(10)-O(5)	1.879(9)	Na(4)-O(33)#4	2.454(13)
W(4)-O(19)	1.921(10)	W(10)-O(19)	1.900(10)	Na(4)-O(41)	2.481(16)
W(4)-O(7)	1.963(9)	W(10)-O(14)#1	1.994(9)	Na(4)-O(40)#5	2.575(15)
W(4)-O(4)	1.995(10)	W(10)-O(14)	2.013(8)	Na(4)-O(46)	2.604(17)
W(4)-O(21)	2.146(9)	W(10)-O(17)	2.109(13)	Na(4)-O(36)#5	2.608(14)
W(5)-O(33)	1.733(10)	W(10)-O(3)#1	2.169(14)	Na(4)-O(43)	2.623(17)
W(5)-O(31)	1.879(10)	Zn(1)-O(24)	1.923(9)	Na(4)-Na(1)#5	3.723(11)
W(5)-O(15)	1.933(10)	Zn(1)-O(23)	1.923(9)	Na(5)-O(45)	2.384(16)
W(5)-O(22)	1.946(11)	Zn(1)-O(21)	1.933(8)	Na(5)-O(2)#1	2.385(14)
W(5)-O(29)	1.963(10)	Zn(1)-O(14)	1.951(9)	Na(5)-O(54)	2.37(4)
W(5)-O(24)	2.214(9)	Mn(1)-O(13)#1	2.083(15)	Na(5)-O(42)	2.405(13)
W(6)-O(34)	1.747(11)	Mn(1)-O(27)#1	2.091(12)	Na(5)-O(50)	2.54(2)
W(6)-O(3)	1.889(11)	Mn(1)-O(14)#1	2.091(10)	Na(5)-O(38)	2.570(15)
W(6)-O(28)	1.912(9)	Mn(1)-O(35)	2.156(12)	Na(6)-O(47)	2.24(3)
W(6)-O(20)	1.954(10)	Mn(1)-O(3)	2.161(11)	Na(6)-O(52)	2.40(4)
W(6)-O(15)	1.988(10)	Mn(1)-O(17)	2.203(11)	Na(6)-O(53)	2.40(4)
W(6)-O(24)	2.136(9)	Na(1)-O(47)	2.292(16)	Na(6)-O(51)	2.79(3)
W(7)-O(8)	1.739(11)	Na(1)-O(36)	2.338(13)		

Table S4. Selected angles ($^{\circ}$) for { $\text{Na}_{12}\text{Mn}_2\text{Zn}_3\text{W}_{19}$ }.

Bond angles	($^{\circ}$)	Bond angles	($^{\circ}$)
O(12)-W(1)-O(17)	102.7(6)	O(35)-Mn(1)-O(17)	102.2(5)
O(12)-W(1)-O(4)	99.3(5)	O(3)-Mn(1)-O(17)	82.6(4)
O(17)-W(1)-O(4)	89.9(5)	W(3)-O(1)-W(7)	156.5(6)
O(12)-W(1)-O(28)	100.7(5)	W(3)-O(2)-Na(5)#1	140.3(7)
O(17)-W(1)-O(28)	86.8(4)	W(6)-O(3)-Mn(1)	124.4(7)
O(4)-W(1)-O(28)	160.0(4)	W(6)-O(3)-Zn(2)#1	136.8(7)
O(12)-W(1)-O(9)	95.4(5)	Mn(1)-O(3)-Zn(2)#1	96.5(4)
O(17)-W(1)-O(9)	161.8(5)	W(6)-O(3)-W(10)#1	136.8(7)
O(4)-W(1)-O(9)	89.3(5)	Mn(1)-O(3)-W(10)#1	96.5(4)
O(28)-W(1)-O(9)	87.8(4)	Zn(2)#1-O(3)-W(10)#1	0.00(3)
O(12)-W(1)-O(21)	168.1(4)	W(1)-O(4)-W(4)	112.1(4)
O(17)-W(1)-O(21)	88.1(4)	W(1)-O(4)-Na(3)	127.9(5)
O(4)-W(1)-O(21)	75.4(4)	W(4)-O(4)-Na(3)	118.2(4)
O(28)-W(1)-O(21)	84.8(4)	W(10)-O(5)-W(3)#1	145.9(6)
O(9)-W(1)-O(21)	74.1(4)	W(4)-O(7)-W(8)	111.1(4)
O(26)-W(2)-O(25)	100.4(5)	W(4)-O(7)-Na(6)	133.4(7)
O(26)-W(2)-O(16)	100.6(5)	W(8)-O(7)-Na(6)	113.3(7)
O(25)-W(2)-O(16)	96.3(5)	W(1)-O(9)-W(8)	113.8(5)
O(26)-W(2)-O(31)	98.6(5)	W(9)-O(11)-W(7)	111.7(5)
O(25)-W(2)-O(31)	159.6(4)	W(1)-O(12)-Na(2)	139.6(6)
O(16)-W(2)-O(31)	87.2(4)	W(9)-O(13)-Mn(1)#1	134.9(8)
O(26)-W(2)-O(18)	98.3(5)	Zn(1)-O(14)-Zn(2)#1	114.9(4)
O(25)-W(2)-O(18)	88.1(4)	Zn(1)-O(14)-W(10)#1	114.9(4)
O(16)-W(2)-O(18)	159.5(4)	Zn(2)#1-O(14)-W(10)#1	0.00(6)
O(31)-W(2)-O(18)	82.1(4)	Zn(1)-O(14)-W(10)	113.6(4)
O(26)-W(2)-O(23)	173.3(4)	Zn(2)#1-O(14)-W(10)	102.9(4)
O(25)-W(2)-O(23)	75.2(4)	W(10)#1-O(14)-W(10)	102.9(4)
O(16)-W(2)-O(23)	75.3(4)	Zn(1)-O(14)-Mn(1)#1	116.9(4)
O(31)-W(2)-O(23)	86.4(4)	Zn(2)#1-O(14)-Mn(1)#1	103.0(4)
O(18)-W(2)-O(23)	86.7(4)	W(10)#1-O(14)-Mn(1)#1	103.0(4)
O(2)-W(3)-O(1)	103.3(5)	W(10)-O(14)-Mn(1)#1	103.8(4)
O(2)-W(3)-O(5)#1	101.2(5)	W(5)-O(15)-W(6)	113.7(5)
O(1)-W(3)-O(5)#1	89.3(5)	W(2)-O(16)-W(7)	113.4(5)
O(2)-W(3)-O(20)	96.5(5)	W(1)-O(17)-W(10)	135.8(6)
O(1)-W(3)-O(20)	160.2(4)	W(1)-O(17)-Mn(1)	126.1(6)
O(5)#1-W(3)-O(20)	86.8(5)	W(10)-O(17)-Mn(1)	95.8(5)
O(2)-W(3)-O(29)	96.2(5)	W(8)-O(18)-W(2)	154.3(6)
O(1)-W(3)-O(29)	90.6(5)	W(10)-O(19)-W(4)	145.1(5)
O(5)#1-W(3)-O(29)	162.2(4)	W(6)-O(20)-W(3)	112.6(5)
O(20)-W(3)-O(29)	87.3(5)	Zn(1)-O(21)-W(4)	116.0(4)
O(2)-W(3)-O(24)	167.6(5)	Zn(1)-O(21)-W(8)	122.2(4)

O(1)-W(3)-O(24)	86.5(4)	W(4)-O(21)-W(8)	98.0(3)
O(5)#1-W(3)-O(24)	86.3(4)	Zn(1)-O(21)-W(1)	120.5(4)
O(20)-W(3)-O(24)	74.0(4)	W(4)-O(21)-W(1)	97.1(3)
O(29)-W(3)-O(24)	75.9(4)	W(8)-O(21)-W(1)	97.9(3)
O(10)-W(4)-O(32)	100.6(5)	W(8)-O(22)-W(5)	146.7(6)
O(10)-W(4)-O(19)	101.4(5)	Zn(1)-O(23)-W(9)	119.0(5)
O(32)-W(4)-O(19)	90.4(4)	Zn(1)-O(23)-W(7)	117.1(5)
O(10)-W(4)-O(7)	96.4(5)	W(9)-O(23)-W(7)	97.9(4)
O(32)-W(4)-O(7)	91.7(4)	Zn(1)-O(23)-W(2)	121.3(5)
O(19)-W(4)-O(7)	161.4(4)	W(9)-O(23)-W(2)	98.3(4)
O(10)-W(4)-O(4)	95.7(4)	W(7)-O(23)-W(2)	98.6(4)
O(32)-W(4)-O(4)	163.7(4)	Zn(1)-O(24)-W(6)	119.3(4)
O(19)-W(4)-O(4)	85.9(4)	Zn(1)-O(24)-W(3)	116.9(4)
O(7)-W(4)-O(4)	86.9(4)	W(6)-O(24)-W(3)	98.1(3)
O(10)-W(4)-O(21)	168.0(4)	Zn(1)-O(24)-W(5)	122.8(4)
O(32)-W(4)-O(21)	89.1(4)	W(6)-O(24)-W(5)	98.0(4)
O(19)-W(4)-O(21)	85.6(4)	W(3)-O(24)-W(5)	96.7(3)
O(7)-W(4)-O(21)	76.0(4)	W(2)-O(25)-W(9)	113.6(5)
O(4)-W(4)-O(21)	74.9(3)	W(7)-O(27)-Mn(1)#1	135.9(7)
O(33)-W(5)-O(31)	101.5(5)	W(6)-O(28)-W(1)	154.3(6)
O(33)-W(5)-O(15)	98.7(5)	W(5)-O(29)-W(3)	112.1(5)
O(31)-W(5)-O(15)	159.6(4)	W(5)-O(31)-W(2)	156.0(6)
O(33)-W(5)-O(22)	99.0(5)	W(4)-O(32)-W(9)	154.0(6)
O(31)-W(5)-O(22)	86.9(4)	W(5)-O(33)-Na(4)#2	143.3(6)
O(15)-W(5)-O(22)	86.7(4)	Mn(1)-O(35)-Na(2)	127.7(6)
O(33)-W(5)-O(29)	97.8(5)	O(47)-Na(1)-O(36)	171.5(7)
O(31)-W(5)-O(29)	89.9(5)	O(47)-Na(1)-O(40)	95.4(6)
O(15)-W(5)-O(29)	90.6(5)	O(36)-Na(1)-O(40)	78.9(5)
O(22)-W(5)-O(29)	163.2(4)	O(47)-Na(1)-O(37)	98.1(6)
O(33)-W(5)-O(24)	169.4(4)	O(36)-Na(1)-O(37)	88.9(5)
O(31)-W(5)-O(24)	86.7(4)	O(40)-Na(1)-O(37)	162.0(5)
O(15)-W(5)-O(24)	73.7(4)	O(47)-Na(1)-O(51)	83.2(9)
O(22)-W(5)-O(24)	88.1(4)	O(36)-Na(1)-O(51)	102.1(8)
O(29)-W(5)-O(24)	75.2(4)	O(40)-Na(1)-O(51)	83.1(7)
O(34)-W(6)-O(3)	102.7(7)	O(37)-Na(1)-O(51)	86.6(7)
O(34)-W(6)-O(28)	99.5(5)	O(47)-Na(1)-O(39)	86.1(7)
O(3)-W(6)-O(28)	89.2(4)	O(36)-Na(1)-O(39)	89.3(5)
O(34)-W(6)-O(20)	97.9(5)	O(40)-Na(1)-O(39)	104.3(5)
O(3)-W(6)-O(20)	88.6(5)	O(37)-Na(1)-O(39)	88.6(5)
O(28)-W(6)-O(20)	162.6(4)	O(51)-Na(1)-O(39)	167.6(8)
O(34)-W(6)-O(15)	94.3(6)	O(48)-Na(2)-O(41)	98.9(6)
O(3)-W(6)-O(15)	162.8(5)	O(48)-Na(2)-O(49)	103.8(8)
O(28)-W(6)-O(15)	90.7(4)	O(41)-Na(2)-O(49)	151.7(7)
O(20)-W(6)-O(15)	86.3(5)	O(48)-Na(2)-O(12)	97.1(6)

O(34)-W(6)-O(24)	166.6(5)	O(41)-Na(2)-O(12)	99.6(5)
O(3)-W(6)-O(24)	88.3(5)	O(49)-Na(2)-O(12)	94.1(6)
O(28)-W(6)-O(24)	88.0(4)	O(48)-Na(2)-O(43)	83.8(7)
O(20)-W(6)-O(24)	74.6(4)	O(41)-Na(2)-O(43)	80.0(5)
O(15)-W(6)-O(24)	74.5(4)	O(49)-Na(2)-O(43)	85.9(6)
O(8)-W(7)-O(27)	103.0(5)	O(12)-Na(2)-O(43)	179.0(6)
O(8)-W(7)-O(1)	101.0(5)	O(48)-Na(2)-O(35)	173.0(6)
O(27)-W(7)-O(1)	94.0(5)	O(41)-Na(2)-O(35)	74.1(4)
O(8)-W(7)-O(11)	97.8(5)	O(49)-Na(2)-O(35)	82.7(7)
O(27)-W(7)-O(11)	92.1(5)	O(12)-Na(2)-O(35)	84.7(5)
O(1)-W(7)-O(11)	158.4(4)	O(43)-Na(2)-O(35)	94.4(5)
O(8)-W(7)-O(16)	90.4(5)	O(38)-Na(3)-O(39)	101.0(5)
O(27)-W(7)-O(16)	166.2(5)	O(38)-Na(3)-O(45)	82.7(5)
O(1)-W(7)-O(16)	86.5(4)	O(39)-Na(3)-O(45)	172.7(6)
O(11)-W(7)-O(16)	82.8(4)	O(38)-Na(3)-O(42)	82.4(5)
O(8)-W(7)-O(23)	161.4(4)	O(39)-Na(3)-O(42)	93.8(5)
O(27)-W(7)-O(23)	93.6(5)	O(45)-Na(3)-O(42)	80.4(5)
O(1)-W(7)-O(23)	86.1(4)	O(38)-Na(3)-O(37)	168.6(5)
O(11)-W(7)-O(23)	72.8(4)	O(39)-Na(3)-O(37)	90.2(5)
O(16)-W(7)-O(23)	72.7(4)	O(45)-Na(3)-O(37)	85.9(5)
O(30)-W(8)-O(18)	101.3(5)	O(42)-Na(3)-O(37)	94.7(5)
O(30)-W(8)-O(22)	100.7(5)	O(38)-Na(3)-O(4)	93.4(4)
O(18)-W(8)-O(22)	87.8(4)	O(39)-Na(3)-O(4)	84.4(4)
O(30)-W(8)-O(9)	96.9(5)	O(45)-Na(3)-O(4)	101.8(5)
O(18)-W(8)-O(9)	161.8(4)	O(42)-Na(3)-O(4)	175.0(5)
O(22)-W(8)-O(9)	88.4(4)	O(37)-Na(3)-O(4)	90.0(4)
O(30)-W(8)-O(7)	94.7(5)	O(44)-Na(4)-O(33)#4	79.8(5)
O(18)-W(8)-O(7)	89.7(4)	O(44)-Na(4)-O(41)	163.0(6)
O(22)-W(8)-O(7)	164.7(4)	O(33)#4-Na(4)-O(41)	102.4(5)
O(9)-W(8)-O(7)	89.2(4)	O(44)-Na(4)-O(40)#5	116.5(6)
O(30)-W(8)-O(21)	165.9(4)	O(33)#4-Na(4)-O(40)#5	80.2(4)
O(18)-W(8)-O(21)	88.1(4)	O(41)-Na(4)-O(40)#5	80.3(4)
O(22)-W(8)-O(21)	90.1(4)	O(44)-Na(4)-O(46)	87.7(6)
O(9)-W(8)-O(21)	74.1(4)	O(33)#4-Na(4)-O(46)	149.5(5)
O(7)-W(8)-O(21)	74.7(3)	O(41)-Na(4)-O(46)	82.1(5)
O(6)-W(9)-O(13)	103.0(6)	O(40)#5-Na(4)-O(46)	130.0(5)
O(6)-W(9)-O(11)	99.1(6)	O(44)-Na(4)-O(36)#5	78.9(5)
O(13)-W(9)-O(11)	94.6(5)	O(33)#4-Na(4)-O(36)#5	131.0(5)
O(6)-W(9)-O(32)	98.4(6)	O(41)-Na(4)-O(36)#5	110.4(5)
O(13)-W(9)-O(32)	91.4(5)	O(40)#5-Na(4)-O(36)#5	71.0(4)
O(11)-W(9)-O(32)	159.8(4)	O(46)-Na(4)-O(36)#5	72.2(5)
O(6)-W(9)-O(25)	90.6(5)	O(44)-Na(4)-O(43)	90.4(5)
O(13)-W(9)-O(25)	166.4(5)	O(33)#4-Na(4)-O(43)	76.7(5)
O(11)-W(9)-O(25)	83.8(4)	O(41)-Na(4)-O(43)	74.0(5)

O(32)-W(9)-O(25)	85.9(4)	O(40)#5-Na(4)-O(43)	140.5(5)
O(6)-W(9)-O(23)	162.7(5)	O(46)-Na(4)-O(43)	75.6(5)
O(13)-W(9)-O(23)	93.6(5)	O(36)#5-Na(4)-O(43)	146.4(5)
O(11)-W(9)-O(23)	74.4(4)	O(45)-Na(5)-O(2)#1	85.0(6)
O(32)-W(9)-O(23)	85.9(4)	O(45)-Na(5)-O(54)	162.7(14)
O(25)-W(9)-O(23)	72.9(4)	O(2)#1-Na(5)-O(54)	93.6(12)
O(5)-W(10)-O(19)	97.6(4)	O(45)-Na(5)-O(42)	81.4(5)
O(5)-W(10)-O(14)#1	95.0(4)	O(2)#1-Na(5)-O(42)	162.0(5)
O(19)-W(10)-O(14)#1	165.5(4)	O(54)-Na(5)-O(42)	96.0(12)
O(5)-W(10)-O(14)	163.9(4)	O(45)-Na(5)-O(50)	83.3(7)
O(19)-W(10)-O(14)	92.2(4)	O(2)#1-Na(5)-O(50)	108.0(6)
O(14)#1-W(10)-O(14)	77.1(4)	O(54)-Na(5)-O(50)	113.4(14)
O(5)-W(10)-O(17)	97.4(4)	O(42)-Na(5)-O(50)	82.1(6)
O(19)-W(10)-O(17)	89.4(4)	O(45)-Na(5)-O(38)	78.6(5)
O(14)#1-W(10)-O(17)	82.0(4)	O(2)#1-Na(5)-O(38)	87.0(5)
O(14)-W(10)-O(17)	95.4(4)	O(54)-Na(5)-O(38)	84.1(14)
O(5)-W(10)-O(3)#1	87.1(4)	O(42)-Na(5)-O(38)	78.8(5)
O(19)-W(10)-O(3)#1	95.1(4)	O(50)-Na(5)-O(38)	155.4(7)
O(14)#1-W(10)-O(3)#1	92.6(4)	O(47)-Na(6)-O(52)	107.5(11)
O(14)-W(10)-O(3)#1	79.4(4)	O(47)-Na(6)-O(53)	141.4(13)
O(17)-W(10)-O(3)#1	173.2(4)	O(52)-Na(6)-O(53)	108.7(14)
O(24)-Zn(1)-O(23)	108.0(4)	O(47)-Na(6)-O(7)	81.0(7)
O(24)-Zn(1)-O(21)	103.8(4)	O(52)-Na(6)-O(7)	122.2(12)
O(23)-Zn(1)-O(21)	107.3(4)	O(53)-Na(6)-O(7)	90.7(11)
O(24)-Zn(1)-O(14)	113.8(4)	O(47)-Na(6)-O(51)	76.2(9)
O(23)-Zn(1)-O(14)	109.4(4)	O(52)-Na(6)-O(51)	96.0(10)
O(21)-Zn(1)-O(14)	114.1(4)	O(53)-Na(6)-O(51)	87.2(10)
O(13)#1-Mn(1)-O(27)#1	91.6(5)	O(7)-Na(6)-O(51)	140.1(10)
O(13)#1-Mn(1)-O(14)#1	94.1(4)	Na(1)-O(36)-Na(4)#3	97.5(5)
O(27)#1-Mn(1)-O(14)#1	93.4(4)	Na(1)-O(37)-Na(3)	90.4(5)
O(13)#1-Mn(1)-O(35)	85.9(5)	Na(3)-O(38)-Na(5)	81.5(4)
O(27)#1-Mn(1)-O(35)	93.1(4)	Na(3)-O(39)-Na(1)	90.7(5)
O(14)#1-Mn(1)-O(35)	173.5(4)	Na(1)-O(40)-Na(4)#3	96.9(5)
O(13)#1-Mn(1)-O(3)	93.7(5)	Na(2)-O(41)-Na(4)	107.2(6)
O(27)#1-Mn(1)-O(3)	170.1(5)	Na(5)-O(42)-Na(3)	83.3(4)
O(14)#1-Mn(1)-O(3)	77.9(5)	Na(2)-O(43)-Na(4)	98.5(5)
O(35)-Mn(1)-O(3)	95.6(5)	Na(5)-O(45)-Na(3)	84.7(5)
O(13)#1-Mn(1)-O(17)	171.4(5)	Na(6)-O(47)-Na(1)	100.5(10)
O(27)#1-Mn(1)-O(17)	90.9(5)	Na(1)-O(51)-Na(6)	83.5(8)
O(14)#1-Mn(1)-O(17)	77.6(4)		

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