Supporting Information for

The synergistic effect of $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$ cores and peripheral metal sites in catalytic oxidative cyclization of acetylacetone

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Experimental Section

All of the chemicals were obtained from commercial sources and were used without further purification, except $K_{12}[WZn(VO)_2(ZnW_9O_{34})_2]\cdot 26H_2O$ (abbreviated as $K_{12}\{V_2Zn_3W_{19}\}$), and $Na_{12}[WZn\{Zn(H_2O)\}_2(ZnW_9O_{34})_2]\cdot 46H_2O$ (abbreviated as $Na_{12}\{Zn_5W_{19}\}$) were synthesized according to the literatures.[1] IR spectra were recorded on KBr pellets with a FTS-40 spectrophotometer. Thermogravimetric analyses (TGA) were carried out under N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 ^oC min^{-1}. Powder X-ray diffraction data (PXRD) were recorded on a RIGAKU D/MAX 2550/PC for Cu-Kα (λ = 1.5406 Å). ^1H NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported relative to internal standard TMS (0 ppm).

Single crystal X-ray data collections and structure determinations

The determinations of the unit cells and data collections for the crystals of compounds **1**, **2**, **3**, **I** and **II** were performed on a CrysAlisPro, Oxford Diffraction Ltd. The data of **1**, **2** and **3** were collected using graphite–monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data of **I** and **II** were collected using graphite–monochromatic Cu radiation (λ = 1.54178 Å) at 293 K. The data sets were corrected by empirical absorption correction.[2] The structures were solved by direct methods, and refined by full-matrix least-square methods with the **SHELX-97** program package.[3] All non-hydrogen atoms including solvent molecules were located successfully from Fourier maps and were refined anisotropically.

References:

1. C. M. Tourné, G. F. Tourné, F. Zonnevijlle, *J. Chem. Soc., Dalton Trans.*1991, 143.

2. Oxford Diffraction Ltd. *CrysAlisPro*, Version 1.171.33.56, 2010.

3. G. M. Sheldrick, Program for Structure Refinement, University of Göttingen, Germany, 1997.

Tables:

Table S1. Crystal data and structure refinements for **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$H_{74}Mn_4O_{105}V_2W_{19}Zn_3$	$H_{104}Co_4K_2O_{121}V_2W_{19}Zn_3$	$H_{98}K_2Ni_4O_{118}V_2W_{19}Zn_3$
Formula weight	5765.49	6145.89	6090.96
Crystal size /mm^3	0.38 × 0.29 × 0.21	0.35 × 0.21 × 0.19	0.19 × 0.11 × 0.09
Crystal color	Deep brown	Deep red	Deep green
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	C2/c
a /Å	12.5382(3)	32.2388(9)	32.1482(9)
b / Å	13.9382(4)	14.6184(5)	14.5862(4)
c / Å	16.7244(5)	21.7787(7)	21.7639(6)
α /^{o}	84.004(2)	90	90
β /^{o}	73.969(2)	95.935(2)	96.069(2)
γ /^{o}	63.604(3)	90	90
Volume /Å^3	2515.66(12)	10208.8(6)	10148.3(5)
Z	1	4	4
ρ_{calcd} /g cm^{-3}	3.806	3.999	3.987
μ /mm^{-1}	23.092	23.020	23.242
F(000)	2556	11040	10936
θ range /^{o}	3.48 to 26.38	3.47 to 26.45	3.15 to 26.37
Limiting indices	$-15 \le h \le 15$ $-16 \le k \le 17$ $-20 \le l \le 20$	$-31 \le h \le 39$ $-18 \le k \le 16$ $-27 \le l \le 23$	$-39 \le h \le 40$ $-16 \le k \le 18$ $-27 \le l \le 27$
Reflections collected	8157	33261	50152
R(int)	0.0453	0.0564	0.0411
Data / parameters	10260 / 610	10379 / 685	10359 / 658
GOF on F^2	1.332	1.221	1.150
$R_1(wR_2)$ [$I > 2\sigma(I)$]	0.0967 (0.2451)	0.0667 (0.1608)	0.0649 (0.1604)
$R_1(wR_2)$ [all data]	0.1143 (0.2512)	0.0812 (0.1651)	0.0794 (0.1646)

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$

Table S2. Crystal data and structure refinements for **I** and **II**.

Compound	**I**	**II**
Empirical formula	$C_8H_{10}O_4$	$C_{10}H_{14}O_5$
Formula weight	170.16	214.21
Crystal size /mm	0.21 × 0.18 × 0.12	0.23 × 0.21 × 0.11
Crystal color	Colorless	Colorless
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a /Å	8.1260(12)	7.4227(4)
b / Å	13.048(2)	8.4007(6)
c / Å	8.6210(15)	9.1488(6)
α /°	90	85.546(6)
β /°	113.676(15)	69.109(6)
γ /°	90	81.652(5)
Volume /Å^3	837.1(2)	527.12(6)
Z	4	2
ρ_{calcd} /g cm^{-3}	1.350	1.350
F(000)	360	228
μ /mm^{-1}	0.928	0.921
θ range /°	5.95 to 67.15	5.18 to 67.92
Limiting indices	$-9 \le h \le 9$ $-10 \le k \le 15$ $-6 \le l \le 10$	$-8 \le h \le 7$ $-10 \le k \le 10$ $-10 \le l \le 10$
Reflections collected	3545 [R(int) = 0.0408]	3997 [R(int) = 0.0313]
Data / parameters	1461 / 109	1852 / 136
GOF on F^2	0.989	1.038
$R_1(wR_2)$ $[I > 2\sigma(I)]$	0.0482 (0.1211)	0.0592 (0.1770)
$R_1(wR_2)$ [all data]	0.0726 (0.1342)	0.0767 (0.1930)

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$

Table S3. Bond lengths and bond angles for **I**.

Bond length	(Å)	Bond length	(Å)
O(1)-C(4)	1.329(3)	C(1)-C(7)	1.501(4)
O(1)-C(1)	1.490(3)	C(1)-C(2)	1.524(3)
O(2)-C(1)	1.371(3)	C(2)-C(3)	1.445(3)
C(8)-C(4)	1.474(3)	C(3)-C(4)	1.361(3)
O(4)-C(2)	1.220(3)	C(3)-C(5)	1.474(3)
O(6)-C(5)	1.226(3)	C(5)-C(6)	1.492(4)

Bond angle	(°)	Bond angle	(°)
C(4)-O(1)-C(1)	108.54(16)	C(4)-C(3)-C(2)	107.12(19)
O(2)-C(1)-O(1)	108.3(2)	C(4)-C(3)-C(5)	125.7(2)
O(2)-C(1)-C(7)	115.11(19)	C(2)-C(3)-C(5)	127.1(2)
O(1)-C(1)-C(7)	107.23(19)	O(1)-C(4)-C(3)	114.82(19)
O(2)-C(1)-C(2)	108.9(2)	O(1)-C(4)-C(8)	115.0(2)
O(1)-C(1)-C(2)	102.53(17)	C(3)-C(4)-C(8)	130.1(2)
C(7)-C(1)-C(2)	113.9(2)	O(6)-C(5)-C(3)	120.2(2)
O(4)-C(2)-C(3)	131.1(2)	O(6)-C(5)-C(6)	122.0(2)
O(4)-C(2)-C(1)	122.2(2)	C(3)-C(5)-C(6)	117.8(2)
C(3)-C(2)-C(1)	106.62(19)		

Table S4. Bond lengths and bond angles for **II**.

Bond length	(Å)	Bond length	(Å)
O(1)-C(4)	1.354(3)	C(2)-C(3)	1.509(4)
O(1)-C(1)	1.477(3)	C(2)-C(6)	1.544(4)
O(2)-C(1)	1.387(4)	C(3)-C(4)	1.352(4)
O(3)-C(2)	1.416(3)	C(3)-C(8)	1.441(4)
O(4)-C(6)	1.217(4)	C(4)-C(10)	1.485(4)
O(5)-C(8)	1.238(4)	C(6)-C(7)	1.483(4)
C(1)-C(5)	1.512(4)	C(8)-C(9)	1.503(4)
C(1)-C(2)	1.553(4)		

Bond angle	(^{o})	Bond angle	(^{o})
C(4)-O(1)-C(1)	108.6(2)	C(4)-C(3)-C(8)	130.6(3)
O(2)-C(1)-O(1)	107.0(2)	C(4)-C(3)-C(2)	108.5(2)
O(2)-C(1)-C(5)	113.1(2)	C(8)-C(3)-C(2)	120.6(2)
O(1)-C(1)-C(5)	107.8(2)	C(3)-C(4)-O(1)	113.5(2)
O(2)-C(1)-C(2)	108.8(2)	C(3)-C(4)-C(10)	132.9(3)
O(1)-C(1)-C(2)	103.4(2)	O(1)-C(4)-C(10)	113.7(2)
C(5)-C(1)-C(2)	115.9(2)	O(4)-C(6)-C(7)	122.2(3)
O(3)-C(2)-C(3)	109.2(2)	O(4)-C(6)-C(2)	116.6(3)
O(3)-C(2)-C(6)	107.8(2)	C(7)-C(6)-C(2)	121.2(2)
C(3)-C(2)-C(6)	115.9(2)	O(5)-C(8)-C(3)	118.4(3)
O(3)-C(2)-C(1)	110.5(2)	O(5)-C(8)-C(9)	119.8(3)
C(3)-C(2)-C(1)	102.0(2)	C(3)-C(8)-C(9)	121.7(3)
C(6)-C(2)-C(1)	111.3(2)		

Table S5. Selected bond lengths for **1**.

Bond length	(Å)	Bond length	(Å)	Bond length	(Å)
W(1)-O(33)	1.739(19)	W(5)-O(20)	2.01(3)	W(10)-O(25)^i	1.93(3)
W(1)-O(28)	1.85(2)	W(5)-O(15)	2.13(2)	W(10)-O(2)	1.97(3)
W(1)-O(22)	1.87(2)	W(6)-O(23)	1.76(2)	W(10)-O(17)	1.99(2)
W(1)-O(13)	1.945(17)	W(6)-O(26)	1.774(19)	W(10)-O(17)^i	2.012(19)
W(1)-O(8)	1.990(18)	W(6)-O(4)	1.96(2)	W(10)-O(7)^i	2.05(2)
W(1)-O(14)	2.238(18)	W(6)-O(16)	1.96(2)	W(10)-O(30)	2.14(2)
W(2)-O(37)	1.71(3)	W(6)-O(28)	2.09(2)	Zn(1)-O(10)	1.89(2)
W(2)-O(2)	1.89(3)	W(6)-O(14)	2.11(2)	Zn(1)-O(15)	1.914(19)
W(2)-O(27)	1.905(19)	W(7)-O(9)	1.72(2)	Zn(1)-O(14)	1.943(18)
W(2)-O(18)	1.99(2)	W(7)-O(8)	1.869(17)	Zn(1)-O(17)	1.971(18)
W(2)-O(11)	2.00(2)	W(7)-O(11)	1.93(2)	V(1)-O(36)	1.630(10)
W(2)-O(10)	2.15(2)	W(7)-O(1)	1.96(2)	V(1)-O(5)	2.06(2)
W(3)-O(21)	1.77(3)	W(7)-O(31)	2.00(2)	V(1)-O(26)	2.09(2)
W(3)-O(12)	1.86(3)	W(7)-O(10)	2.213(19)	V(1)-O(30)^i	2.16(2)
W(3)-O(7)	1.93(2)	W(8)-O(6)	1.72(2)	V(1)-O(7)^i	2.17(2)
W(3)-O(29)	1.94(2)	W(8)-O(1)	1.89(2)	V(1)-O(17)	2.167(18)

W(3)-O(38)	1.94(2)	W(8)-O(13)	1.895(17)	Mn(1)-O(32)^{ii}	2.11(2)
W(3)-O(15)	2.15(2)	W(8)-O(20)	1.92(3)	Mn(1)-O(33)	2.17(2)
W(4)-O(3)	1.67(3)	W(8)-O(29)	1.94(2)	Mn(1)-O(41)	2.19(4)
W(4)-O(30)	1.87(2)	W(8)-O(15)	2.23(2)	Mn(1)-O(42)	2.19(4)
W(4)-O(38)	1.91(2)	W(9)-O(32)	1.76(2)	Mn(1)-O(43)	2.19(4)
W(4)-O(18)	1.93(2)	W(9)-O(5)	1.78(2)	Mn(2)-O(34)	2.11(3)
W(4)-O(31)	1.95(2)	W(9)-O(27)	1.90(2)	Mn(2)-O(40)	2.13(4)
W(4)-O(10)	2.19(2)	W(9)-O(16)	1.94(2)	Mn(2)-O(23)	2.18(2)
W(5)-O(35)	1.73(3)	W(9)-O(22)	2.07(2)	Mn(2)-O(39)	2.19(3)
W(5)-O(4)	1.88(2)	W(9)-O(14)	2.125(19)	Mn(2)-O(44)	2.19(4)
W(5)-O(25)	1.92(2)	W(5)-O(12)	1.99(2)	Mn(2)-O(19)	2.21(3)

Symmetry transformations used to generate equivalent atoms: i: -x, -y, -z; ii: -x, -y, -z-1.

Table S6. Selected bond angles for **1**.

Bond angle	(°)	Bond angle	(°)
O(33)-W(1)-O(28)	100.6(11)	O(8)-W(7)-O(10)	87.7(8)
O(33)-W(1)-O(22)	99.1(10)	O(11)-W(7)-O(10)	75.4(8)
O(28)-W(1)-O(22)	95.2(10)	O(1)-W(7)-O(10)	88.3(9)
O(33)-W(1)-O(13)	99.1(10)	O(31)-W(7)-O(10)	73.6(8)
O(28)-W(1)-O(13)	89.5(9)	O(6)-W(8)-O(1)	100.1(11)
O(22)-W(1)-O(13)	160.1(9)	O(6)-W(8)-O(13)	102.3(9)
O(33)-W(1)-O(8)	98.8(10)	O(1)-W(8)-O(13)	86.5(9)
O(28)-W(1)-O(8)	159.6(9)	O(6)-W(8)-O(20)	95.8(11)
O(22)-W(1)-O(8)	88.1(10)	O(1)-W(8)-O(20)	164.0(10)
O(13)-W(1)-O(8)	81.1(9)	O(13)-W(8)-O(20)	91.2(10)
O(33)-W(1)-O(14)	171.5(9)	O(6)-W(8)-O(29)	96.7(10)
O(28)-W(1)-O(14)	74.9(9)	O(1)-W(8)-O(29)	87.2(9)
O(22)-W(1)-O(14)	74.4(8)	O(13)-W(8)-O(29)	160.7(9)
O(13)-W(1)-O(14)	88.2(7)	O(20)-W(8)-O(29)	89.9(10)
O(8)-W(1)-O(14)	86.7(8)	O(6)-W(8)-O(15)	165.7(9)
O(37)-W(2)-O(2)	99.6(13)	O(1)-W(8)-O(15)	89.2(9)
O(37)-W(2)-O(27)	102.8(11)	O(13)-W(8)-O(15)	88.9(8)
O(2)-W(2)-O(27)	90.4(10)	O(20)-W(8)-O(15)	74.9(9)
O(37)-W(2)-O(18)	98.1(11)	O(29)-W(8)-O(15)	72.8(8)
O(2)-W(2)-O(18)	85.3(10)	O(32)-W(9)-O(5)	101.9(11)
O(27)-W(2)-O(18)	159.1(10)	O(32)-W(9)-O(27)	100.3(11)
O(37)-W(2)-O(11)	97.7(13)	O(5)-W(9)-O(27)	94.0(11)
O(2)-W(2)-O(11)	162.1(11)	O(32)-W(9)-O(16)	97.4(10)
O(27)-W(2)-O(11)	89.9(10)	O(5)-W(9)-O(16)	90.5(10)
O(18)-W(2)-O(11)	88.0(9)	O(27)-W(9)-O(16)	160.4(9)
O(37)-W(2)-O(10)	169.5(11)	O(32)-W(9)-O(22)	94.3(10)
O(2)-W(2)-O(10)	86.9(9)	O(5)-W(9)-O(22)	162.8(10)
O(27)-W(2)-O(10)	85.3(9)	O(27)-W(9)-O(22)	88.7(10)
O(18)-W(2)-O(10)	74.1(9)	O(16)-W(9)-O(22)	81.7(9)
O(11)-W(2)-O(10)	75.3(9)	O(32)-W(9)-O(14)	165.0(10)

O(21)-W(3)-O(12)	99.2(10)	O(5)-W(9)-O(14)	89.9(9)
O(21)-W(3)-O(7)	101.7(10)	O(27)-W(9)-O(14)	87.9(9)
O(12)-W(3)-O(7)	90.5(10)	O(16)-W(9)-O(14)	72.9(8)
O(21)-W(3)-O(29)	97.8(11)	O(22)-W(9)-O(14)	73.2(8)
O(12)-W(3)-O(29)	88.7(10)	O(25)^{i}-W(10)-O(2)	96.2(10)
O(7)-W(3)-O(29)	160.4(10)	O(25)^{i}-W(10)-O(17)	166.6(10)
O(21)-W(3)-O(38)	101.6(10)	O(2)-W(10)-O(17)	95.1(9)
O(12)-W(3)-O(38)	159.1(9)	O(25)^{i}-W(10)-O(17)^{i}	93.8(10)
O(7)-W(3)-O(38)	85.8(9)	O(2)-W(10)-O(17)^{i}	165.9(8)
O(29)-W(3)-O(38)	87.9(9)	O(17)-W(10)-O(17)^{i}	76.5(9)
O(21)-W(3)-O(15)	169.4(10)	O(25)^{i}-W(10)-O(7)^{i}	89.5(10)
O(12)-W(3)-O(15)	73.6(9)	O(2)-W(10)-O(7)^{i}	96.9(9)
O(7)-W(3)-O(15)	86.3(8)	O(17)-W(10)-O(7)^{i}	81.9(8)
O(29)-W(3)-O(15)	74.6(9)	O(17)^{i}-W(10)-O(7)^{i}	93.1(8)
O(38)-W(3)-O(15)	85.7(9)	O(25)^{i}-W(10)-O(30)	95.7(10)
O(3)-W(4)-O(30)	102.0(12)	O(2)-W(10)-O(30)	88.3(9)
O(3)-W(4)-O(38)	103.6(11)	O(17)-W(10)-O(30)	91.9(9)
O(30)-W(4)-O(38)	87.8(10)	O(17)^{i}-W(10)-O(30)	80.7(8)
O(3)-W(4)-O(18)	95.5(11)	O(7)^{i}-W(10)-O(30)	172.2(10)
O(30)-W(4)-O(18)	88.2(10)	O(10)-Zn(1)-O(15)	108.1(10)
O(38)-W(4)-O(18)	160.9(9)	O(10)-Zn(1)-O(14)	108.3(9)
O(3)-W(4)-O(31)	94.8(11)	O(15)-Zn(1)-O(14)	108.6(9)
O(30)-W(4)-O(31)	163.0(10)	O(10)-Zn(1)-O(17)	111.5(8)
O(38)-W(4)-O(31)	90.7(9)	O(15)-Zn(1)-O(17)	111.5(9)
O(18)-W(4)-O(31)	87.7(10)	O(14)-Zn(1)-O(17)	108.8(8)
O(3)-W(4)-O(10)	165.9(9)	O(36)-V(1)-O(5)	92.6(13)
O(30)-W(4)-O(10)	87.7(9)	O(36)-V(1)-O(26)	94.2(14)
O(38)-W(4)-O(10)	86.7(8)	O(5)-V(1)-O(26)	88.4(10)
O(18)-W(4)-O(10)	74.5(9)	O(36)-V(1)-O(30)^{i}	101.1(13)
O(31)-W(4)-O(10)	75.3(8)	O(5)-V(1)-O(30)^{i}	166.1(9)
O(35)-W(5)-O(4)	99.7(13)	O(26)-V(1)-O(30)^{i}	92.5(10)
O(35)-W(5)-O(25)	103.2(14)	O(36)-V(1)-O(7)^{i}	99.6(14)
O(4)-W(5)-O(25)	91.5(10)	O(5)-V(1)-O(7)^{i}	93.4(9)
O(35)-W(5)-O(12)	99.4(13)	O(26)-V(1)-O(7)^{i}	166.0(9)
O(4)-W(5)-O(12)	160.8(10)	O(30)^{i}-V(1)-O(7)^{i}	82.5(9)
O(25)-W(5)-O(12)	85.2(10)	O(36)-V(1)-O(17)	174.6(13)
O(35)-W(5)-O(20)	96.1(13)	O(5)-V(1)-O(17)	89.3(8)
O(4)-W(5)-O(20)	92.0(10)	O(26)-V(1)-O(17)	90.9(9)
O(25)-W(5)-O(20)	159.6(11)	O(30)^{i}-V(1)-O(17)	76.9(8)
O(12)-W(5)-O(20)	85.0(10)	O(7)^{i}-V(1)-O(17)	75.2(8)
O(35)-W(5)-O(15)	167.7(11)	O(24)-Mn(1)-O(32)^{ii}	86.1(10)
O(4)-W(5)-O(15)	89.5(9)	O(24)-Mn(1)-O(33)	176.6(12)
O(25)-W(5)-O(15)	84.5(11)	O(32)^{ii}-Mn(1)-O(33)	95.8(9)
O(12)-W(5)-O(15)	71.4(9)	O(24)-Mn(1)-O(41)	92.4(15)
O(20)-W(5)-O(15)	75.4(9)	O(32)^{ii}-Mn(1)-O(41)	88.2(15)
O(23)-W(6)-O(26)	103.2(11)	O(33)-Mn(1)-O(41)	84.9(14)
O(23)-W(6)-O(4)	97.7(11)	O(24)-Mn(1)-O(42)	95.1(14)
O(26)-W(6)-O(4)	93.2(11)	O(32)^{ii}-Mn(1)-O(42)	87.8(15)

O(23)-W(6)-O(16)	99.2(11)	O(33)-Mn(1)-O(42)	87.7(13)
O(26)-W(6)-O(16)	94.0(10)	O(41)-Mn(1)-O(42)	171.3(17)
O(4)-W(6)-O(16)	159.6(9)	O(24)-Mn(1)-O(43)	94.8(13)
O(23)-W(6)-O(28)	90.6(10)	O(32)^{ii}-Mn(1)-O(43)	179.1(13)
O(26)-W(6)-O(28)	166.1(10)	O(33)-Mn(1)-O(43)	83.2(13)
O(4)-W(6)-O(28)	84.3(9)	O(41)-Mn(1)-O(43)	92(2)
O(16)-W(6)-O(28)	84.2(8)	O(42)-Mn(1)-O(43)	92(2)
O(23)-W(6)-O(14)	162.5(9)	O(34)-Mn(2)-O(40)	92.3(14)
O(26)-W(6)-O(14)	93.1(10)	O(34)-Mn(2)-O(23)	175.5(11)
O(4)-W(6)-O(14)	87.5(8)	O(40)-Mn(2)-O(23)	91.0(12)
O(16)-W(6)-O(14)	73.0(8)	O(34)-Mn(2)-O(39)	94.7(13)
O(28)-W(6)-O(14)	73.2(8)	O(40)-Mn(2)-O(39)	90.5(16)
O(9)-W(7)-O(8)	103.2(10)	O(23)-Mn(2)-O(39)	88.2(11)
O(9)-W(7)-O(11)	95.8(10)	O(34)-Mn(2)-O(44)	89.9(13)
O(8)-W(7)-O(11)	91.3(9)	O(40)-Mn(2)-O(44)	90.8(17)
O(9)-W(7)-O(1)	100.4(10)	O(23)-Mn(2)-O(44)	87.1(11)
O(8)-W(7)-O(1)	86.8(9)	O(39)-Mn(2)-O(44)	175.2(14)
O(11)-W(7)-O(1)	163.7(9)	O(34)-Mn(2)-O(19)	90.9(14)
O(9)-W(7)-O(31)	96.0(10)	O(40)-Mn(2)-O(19)	174.4(14)
O(8)-W(7)-O(31)	160.6(8)	O(23)-Mn(2)-O(19)	86.0(11)
O(11)-W(7)-O(31)	89.0(10)	O(39)-Mn(2)-O(19)	84.7(14)
O(1)-W(7)-O(31)	87.5(10)	O(44)-Mn(2)-O(19)	93.8(14)
O(9)-W(7)-O(10)	166.3(10)		

Symmetry transformations used to generate equivalent atoms: i: -x, -y, -z; ii: -x, -y, -z-1.

Table S7. Selected bond lengths for **2**.

Bond length	(Å)	Bond length	(Å)	Bond length	(Å)
W(1)-O(33)	1.721(12)	W(6)-O(12)	1.931(12)	Co(1)-O(43)	2.064(16)
W(1)-O(37)	1.912(12)	W(6)-O(29)	1.935(11)	Co(1)-O(31)	2.069(14)
W(1)-O(27)^{i}	1.915(11)	W(6)-O(2)	1.979(13)	Co(1)-O(8)	2.075(16)
W(1)-O(35)	1.933(11)	W(6)-O(11)	2.153(13)	Co(1)-O(39)	2.088(19)
W(1)-O(16)	1.968(10)	W(7)-O(15)	1.751(12)	Co(1)-O(38)	2.09(2)
W(1)-O(9)	2.155(12)	W(7)-O(18)	1.811(11)	Co(1)-O(40)	2.127(19)
W(2)-O(25)	1.723(12)	W(7)-O(20)	1.929(13)	Co(2)-O(15)	2.048(12)
W(2)-O(23)	1.851(13)	W(7)-O(28)	1.958(11)	Co(2)-O(4)	2.047(14)
W(2)-O(7)	1.869(12)	W(7)-O(7)	2.085(11)	Co(2)-O(42)	2.071(15)
W(2)-O(32)	1.958(12)	W(7)-O(13)	2.146(12)	Co(2)-O(21)	2.092(16)
W(2)-O(24)	1.960(11)	W(8)-O(3)	1.716(15)	Co(2)-O(41)	2.103(19)
W(2)-O(13)	2.241(11)	W(8)-O(28)	1.873(10)	Co(2)-O(44)	2.127(15)
W(3)-O(31)	1.750(14)	W(8)-O(17)^{i}	1.896(12)	V(1)-O(45)	1.662(9)
W(3)-O(10)	1.798(12)	W(8)-O(36)	1.993(12)	V(1)-O(10)	2.008(14)
W(3)-O(30)	1.932(11)	W(8)-O(37)	2.001(12)	V(1)-O(18)	2.011(13)
W(3)-O(20)	1.991(12)	W(8)-O(9)	2.176(12)	V(1)-O(19)	2.098(12)
W(3)-O(23)	2.082(12)	W(9)-O(26)	1.731(12)	V(1)-O(27)	2.105(12)
W(3)-O(13)	2.104(13)	W(9)-O(22)	1.910(11)	V(1)-O(22)^{i}	2.119(13)

W(4)-O(1)	1.738(13)	W(9)-O(35)	1.918(12)	K(1)-O(46)	2.37(2)
W(4)-O(24)	1.860(11)	W(9)-O(12)	1.938(14)	K(1)-O(48)	2.42(2)
W(4)-O(34)	1.940(12)	W(9)-O(6)	1.975(11)	K(1)-O(26)	2.430(13)
W(4)-O(6)	1.957(12)	W(9)-O(11)	2.140(11)	K(1)-O(50)	2.44(2)
W(4)-O(2)	1.962(14)	W(10)-O(29)	1.901(13)	K(1)-O(33)^{ii}	2.475(14)
W(4)-O(11)	2.206(11)	W(10)-O(17)	1.938(14)	K(1)-O(51)	2.50(2)
W(5)-O(14)	1.755(12)	W(10)-O(19)	2.027(13)	K(1)-O(47)	2.537(16)
W(5)-O(32)	1.870(11)	W(10)-O(19)^{i}	2.037(12)	K(1)-O(49)	2.60(2)
W(5)-O(34)	1.926(12)	W(10)-O(22)	2.062(12)	O(17)-W(8)^{i}	1.896(12)
W(5)-O(36)	1.933(13)	W(10)-O(27)	2.087(13)	O(19)-Zn(2)^{i}	2.037(12)
W(5)-O(16)	1.962(12)	Zn(1)-O(13)	1.912(11)	O(19)-W(10)^{i}	2.037(12)
W(5)-O(9)	2.175(11)	Zn(1)-O(9)	1.916(12)	O(22)-V(1)^{i}	2.119(13)
W(6)-O(5)	1.718(15)	Zn(1)-O(11)	1.916(12)	O(27)-W(1)^{i}	1.915(11)
W(6)-O(30)	1.903(11)	Zn(1)-O(19)	1.923(10)	O(33)-K(1)^{iii}	2.475(14)

Symmetry transformations used to generate equivalent atoms: i: -x+1/2, -y+1/2, -z; ii: -x+1/2, y-1/2, -z+1/2; iii: -x+1/2, y+1/2, -z+1/2.

Table S8. Selected bond angles for **2**.

Bond angle	(°)	Bond angle	(°)
O(33)-W(1)-O(37)	98.9(6)	O(3)-W(8)-O(9)	166.7(6)
O(33)-W(1)-O(27)^{i}	101.9(6)	O(28)-W(8)-O(9)	88.7(5)
O(37)-W(1)-O(27)^{i}	90.0(5)	O(17)^{i}-W(8)-O(9)	86.5(5)
O(33)-W(1)-O(35)	99.8(6)	O(36)-W(8)-O(9)	73.8(5)
O(37)-W(1)-O(35)	161.3(5)	O(37)-W(8)-O(9)	73.1(5)
O(27)^{i}-W(1)-O(35)	86.2(5)	O(26)-W(9)-O(22)	100.9(6)
O(33)-W(1)-O(16)	95.0(6)	O(26)-W(9)-O(35)	101.9(6)
O(37)-W(1)-O(16)	89.2(5)	O(22)-W(9)-O(35)	88.2(5)
O(27)^{i}-W(1)-O(16)	163.0(5)	O(26)-W(9)-O(12)	95.4(6)
O(35)-W(1)-O(16)	89.1(5)	O(22)-W(9)-O(12)	88.8(5)
O(33)-W(1)-O(9)	167.9(5)	O(35)-W(9)-O(12)	162.7(5)
O(37)-W(1)-O(9)	75.3(5)	O(26)-W(9)-O(6)	95.1(5)
O(27)^{i}-W(1)-O(9)	88.9(5)	O(22)-W(9)-O(6)	163.9(5)
O(35)-W(1)-O(9)	86.4(5)	O(35)-W(9)-O(6)	90.1(5)
O(16)-W(1)-O(9)	74.5(4)	O(12)-W(9)-O(6)	88.1(6)
O(25)-W(2)-O(23)	100.2(6)	O(26)-W(9)-O(11)	165.3(5)
O(25)-W(2)-O(7)	97.1(6)	O(22)-W(9)-O(11)	89.1(5)
O(23)-W(2)-O(7)	97.3(6)	O(35)-W(9)-O(11)	89.0(5)
O(25)-W(2)-O(32)	99.4(6)	O(12)-W(9)-O(11)	73.9(5)
O(23)-W(2)-O(32)	159.5(5)	O(6)-W(9)-O(11)	74.8(5)
O(7)-W(2)-O(32)	86.2(6)	O(29)-W(10)-O(17)	95.9(6)
O(25)-W(2)-O(24)	100.4(6)	O(29)-W(10)-O(19)	93.5(5)
O(23)-W(2)-O(24)	88.2(6)	O(17)-W(10)-O(19)	167.7(5)
O(7)-W(2)-O(24)	160.5(5)	O(29)-W(10)-O(19)^{i}	166.9(5)
O(32)-W(2)-O(24)	82.4(5)	O(17)-W(10)-O(19)^{i}	94.4(5)
O(25)-W(2)-O(13)	170.1(6)	O(19)-W(10)-O(19)^{i}	77.5(5)
O(23)-W(2)-O(13)	74.5(5)	O(29)-W(10)-O(22)	91.3(5)

O(7)-W(2)-O(13)	75.6(5)	O(17)-W(10)-O(22)	95.3(5)
O(32)-W(2)-O(13)	86.9(5)	O(19)-W(10)-O(22)	92.4(5)
O(24)-W(2)-O(13)	88.0(5)	O(19)^{i}-W(10)-O(22)	79.8(5)
O(31)-W(3)-O(10)	104.4(6)	O(29)-W(10)-O(27)	94.0(5)
O(31)-W(3)-O(30)	99.7(6)	O(17)-W(10)-O(27)	91.4(5)
O(10)-W(3)-O(30)	94.4(6)	O(19)-W(10)-O(27)	80.0(5)
O(31)-W(3)-O(20)	97.2(6)	O(19)^{i}-W(10)-O(27)	93.7(5)
O(10)-W(3)-O(20)	90.8(6)	O(22)-W(10)-O(27)	171.0(5)
O(30)-W(3)-O(20)	160.5(5)	O(13)-Zn(1)-O(9)	109.6(5)
O(31)-W(3)-O(23)	92.6(6)	O(13)-Zn(1)-O(11)	107.1(5)
O(10)-W(3)-O(23)	162.7(6)	O(9)-Zn(1)-O(11)	107.0(5)
O(30)-W(3)-O(23)	85.4(5)	O(13)-Zn(1)-O(19)	107.4(5)
O(20)-W(3)-O(23)	84.1(5)	O(9)-Zn(1)-O(19)	113.4(5)
O(31)-W(3)-O(13)	163.8(5)	O(11)-Zn(1)-O(19)	112.1(5)
O(10)-W(3)-O(13)	89.5(6)	O(43)-Co(1)-O(31)	90.9(6)
O(30)-W(3)-O(13)	87.2(5)	O(43)-Co(1)-O(8)	178.3(10)
O(20)-W(3)-O(13)	74.0(5)	O(31)-Co(1)-O(8)	88.5(8)
O(23)-W(3)-O(13)	73.3(5)	O(43)-Co(1)-O(39)	89.9(8)
O(1)-W(4)-O(24)	103.2(6)	O(31)-Co(1)-O(39)	96.0(8)
O(1)-W(4)-O(34)	100.0(6)	O(8)-Co(1)-O(39)	91.7(10)
O(24)-W(4)-O(34)	86.7(6)	O(43)-Co(1)-O(38)	92.3(8)
O(1)-W(4)-O(6)	96.0(6)	O(31)-Co(1)-O(38)	87.6(7)
O(24)-W(4)-O(6)	160.4(5)	O(8)-Co(1)-O(38)	86.1(10)
O(34)-W(4)-O(6)	86.2(6)	O(39)-Co(1)-O(38)	175.7(9)
O(1)-W(4)-O(2)	96.6(6)	O(43)-Co(1)-O(40)	90.6(8)
O(24)-W(4)-O(2)	91.3(6)	O(31)-Co(1)-O(40)	175.6(9)
O(34)-W(4)-O(2)	163.3(5)	O(8)-Co(1)-O(40)	89.8(9)
O(6)-W(4)-O(2)	90.3(6)	O(39)-Co(1)-O(40)	88.1(10)
O(1)-W(4)-O(11)	166.1(6)	O(38)-Co(1)-O(40)	88.1(10)
O(24)-W(4)-O(11)	87.9(5)	O(15)-Co(2)-O(4)	88.1(6)
O(34)-W(4)-O(11)	88.8(5)	O(15)-Co(2)-O(42)	93.3(6)
O(6)-W(4)-O(11)	73.7(5)	O(4)-Co(2)-O(42)	178.6(7)
O(2)-W(4)-O(11)	74.6(5)	O(15)-Co(2)-O(21)	90.8(6)
O(14)-W(5)-O(32)	103.0(6)	O(4)-Co(2)-O(21)	91.4(7)
O(14)-W(5)-O(34)	100.5(6)	O(42)-Co(2)-O(21)	88.8(8)
O(32)-W(5)-O(34)	87.8(6)	O(15)-Co(2)-O(41)	90.7(6)
O(14)-W(5)-O(36)	94.8(6)	O(4)-Co(2)-O(41)	87.3(8)
O(32)-W(5)-O(36)	89.8(5)	O(42)-Co(2)-O(41)	92.5(9)
O(34)-W(5)-O(36)	164.7(5)	O(21)-Co(2)-O(41)	178.0(8)
O(14)-W(5)-O(16)	96.0(5)	O(15)-Co(2)-O(44)	176.7(6)
O(32)-W(5)-O(16)	160.9(5)	O(4)-Co(2)-O(44)	88.9(6)
O(34)-W(5)-O(16)	88.1(5)	O(42)-Co(2)-O(44)	89.7(6)
O(36)-W(5)-O(16)	89.3(5)	O(21)-Co(2)-O(44)	87.9(7)
O(14)-W(5)-O(9)	165.7(6)	O(41)-Co(2)-O(44)	90.6(7)
O(32)-W(5)-O(9)	87.2(5)	O(45)-V(1)-O(10)	95.4(7)
O(34)-W(5)-O(9)	89.9(5)	O(45)-V(1)-O(18)	93.9(7)
O(36)-W(5)-O(9)	74.9(5)	O(10)-V(1)-O(18)	89.2(5)
O(16)-W(5)-O(9)	74.2(4)	O(45)-V(1)-O(19)	173.1(6)

O(5)-W(6)-O(30)	100.6(6)	O(10)-V(1)-O(19)	90.7(5)
O(5)-W(6)-O(12)	99.3(6)	O(18)-V(1)-O(19)	89.4(5)
O(30)-W(6)-O(12)	160.1(6)	O(45)-V(1)-O(27)	98.5(6)
O(5)-W(6)-O(29)	100.2(6)	O(10)-V(1)-O(27)	92.3(6)
O(30)-W(6)-O(29)	90.0(5)	O(18)-V(1)-O(27)	167.3(6)
O(12)-W(6)-O(29)	86.1(5)	O(19)-V(1)-O(27)	78.0(5)
O(5)-W(6)-O(2)	97.7(6)	O(45)-V(1)-O(22)^{i}	96.8(6)
O(30)-W(6)-O(2)	89.9(5)	O(10)-V(1)-O(22)^{i}	167.8(5)
O(12)-W(6)-O(2)	87.9(5)	O(18)-V(1)-O(22)^{i}	91.2(5)
O(29)-W(6)-O(2)	161.9(6)	O(19)-V(1)-O(22)^{i}	77.1(5)
O(5)-W(6)-O(11)	170.2(5)	O(27)-V(1)-O(22)^{i}	84.7(5)
O(30)-W(6)-O(11)	86.6(5)	O(46)-K(1)-O(48)	141.8(8)
O(12)-W(6)-O(11)	73.7(5)	O(46)-K(1)-O(26)	140.1(7)
O(29)-W(6)-O(11)	86.5(5)	O(48)-K(1)-O(26)	73.2(6)
O(2)-W(6)-O(11)	75.5(5)	O(46)-K(1)-O(50)	75.9(8)
O(15)-W(7)-O(18)	105.2(6)	O(48)-K(1)-O(50)	107.7(8)
O(15)-W(7)-O(20)	96.4(6)	O(26)-K(1)-O(50)	73.8(6)
O(18)-W(7)-O(20)	93.6(6)	O(46)-K(1)-O(33)^{ii}	77.2(7)
O(15)-W(7)-O(28)	99.3(6)	O(48)-K(1)-O(33)^{ii}	77.9(6)
O(18)-W(7)-O(28)	91.5(6)	O(26)-K(1)-O(33)^{ii}	141.2(5)
O(20)-W(7)-O(28)	161.7(5)	O(50)-K(1)-O(33)^{ii}	140.8(6)
O(15)-W(7)-O(7)	92.7(5)	O(46)-K(1)-O(51)	75.7(8)
O(18)-W(7)-O(7)	162.0(5)	O(48)-K(1)-O(51)	142.2(7)
O(20)-W(7)-O(7)	85.3(5)	O(26)-K(1)-O(51)	75.2(6)
O(28)-W(7)-O(7)	84.5(5)	O(50)-K(1)-O(51)	82.6(8)
O(15)-W(7)-O(13)	163.8(5)	O(33)^{ii}-K(1)-O(51)	117.3(6)
O(18)-W(7)-O(13)	88.7(5)	O(46)-K(1)-O(47)	118.6(7)
O(20)-W(7)-O(13)	74.3(5)	O(48)-K(1)-O(47)	82.4(6)
O(28)-W(7)-O(13)	88.2(5)	O(26)-K(1)-O(47)	75.0(5)
O(7)-W(7)-O(13)	73.7(4)	O(50)-K(1)-O(47)	142.5(7)
O(3)-W(8)-O(28)	102.1(7)	O(33)^{ii}-K(1)-O(47)	76.1(5)
O(3)-W(8)-O(17)^{i}	101.0(7)	O(51)-K(1)-O(47)	69.7(7)
O(28)-W(8)-O(17)^{i}	90.9(6)	O(46)-K(1)-O(49)	77.2(7)
O(3)-W(8)-O(36)	97.8(6)	O(48)-K(1)-O(49)	68.2(7)
O(28)-W(8)-O(36)	91.7(5)	O(26)-K(1)-O(49)	117.0(6)
O(17)^{i}-W(8)-O(36)	160.0(6)	O(50)-K(1)-O(49)	73.1(7)
O(3)-W(8)-O(37)	96.4(6)	O(33)^{ii}-K(1)-O(49)	73.6(6)
O(28)-W(8)-O(37)	161.5(5)	O(51)-K(1)-O(49)	147.1(7)
O(17)^{i}-W(8)-O(37)	85.1(5)	O(47)-K(1)-O(49)	141.3(7)
O(36)-W(8)-O(37)	86.2(5)		

Symmetry transformations used to generate equivalent atoms: i: -x+1/2, -y+1/2, -z; ii: -x+1/2, y-1/2, -z+1/2; iii: -x+1/2, y+1/2, -z+1/2.

Table S9. Selected bond lengths for **3**.

Bond length	(Å)	Bond length	(Å)	Bond length	(Å)
W(1)-O(33)	1.723(13)	W(6)-O(29)	1.916(12)	Zn(1)-O(11)	1.915(11)
W(1)-O(37)	1.914(12)	W(6)-O(30)	1.924(12)	Zn(1)-O(19)	1.923(11)
W(1)-O(35)	1.916(11)	W(6)-O(12)	1.927(11)	Zn(1)-O(9)	1.925(12)
W(1)-O(27)^{i}	1.929(11)	W(6)-O(5)	1.731(15)	Zn(1)-O(13)	1.932(11)
W(1)-O(16)	1.974(12)	W(6)-O(2)	1.987(12)	Ni(1)-O(31)	2.026(13)
W(1)-O(9)	2.161(12)	W(6)-O(11)	2.158(12)	Ni(1)-O(43)	2.034(17)
W(2)-O(25)	1.739(13)	W(7)-O(15)	1.759(12)	Ni(1)-O(8)	2.042(19)
W(2)-O(7)	1.882(12)	W(7)-O(18)	1.819(12)	Ni(1)-O(40)	2.066(18)
W(2)-O(23)	1.882(12)	W(7)-O(28)	1.954(11)	Ni(1)-O(38)	2.071(18)
W(2)-O(24)	1.955(11)	W(7)-O(20)	1.958(12)	Ni(1)-O(39)	2.073(18)
W(2)-O(32)	1.963(12)	W(7)-O(7)	2.080(12)	Ni(2)-O(15)	2.010(12)
W(2)-O(13)	2.212(12)	W(7)-O(13)	2.133(12)	Ni(2)-O(4)	2.023(15)
W(3)-O(31)	1.757(13)	W(8)-O(3)	1.727(14)	Ni(2)-O(42)	2.044(15)
W(3)-O(10)	1.803(12)	W(8)-O(28)	1.876(10)	Ni(2)-O(41)	2.055(16)
W(3)-O(30)	1.927(12)	W(8)-O(17)^{i}	1.899(13)	Ni(2)-O(44)	2.074(15)
W(3)-O(20)	1.968(12)	W(8)-O(36)	1.990(11)	Ni(2)-O(21)	2.086(15)
W(3)-O(23)	2.044(12)	W(8)-O(37)	2.000(12)	V(1)-O(45)	1.654(9)
W(3)-O(13)	2.121(12)	W(8)-O(9)	2.170(12)	V(1)-O(18)	1.998(12)
W(4)-O(1)	1.729(15)	W(9)-O(26)	1.719(13)	V(1)-O(10)	2.004(13)
W(4)-O(24)	1.878(11)	W(9)-O(22)	1.902(11)	V(1)-O(19)	2.095(12)
W(4)-O(34)	1.933(11)	W(9)-O(35)	1.926(11)	V(1)-O(27)	2.099(12)
W(4)-O(6)	1.939(13)	W(9)-O(12)	1.938(12)	V(1)-O(22)^{i}	2.110(13)
W(4)-O(2)	1.954(12)	W(9)-O(6)	1.978(12)	K(1)-O(46)	2.41(2)
W(4)-O(11)	2.210(11)	W(9)-O(11)	2.136(11)	K(1)-O(48)	2.42(2)
W(5)-O(14)	1.757(12)	W(10)-O(29)	1.909(13)	K(1)-O(26)	2.448(14)
W(5)-O(32)	1.866(11)	W(10)-O(17)	1.936(14)	K(1)-O(50)	2.448(19)
W(5)-O(34)	1.926(12)	W(10)-O(19)^{i}	2.026(13)	K(1)-O(33)^{iii}	2.457(14)
W(5)-O(36)	1.959(12)	W(10)-O(19)	2.037(13)	K(1)-O(51)	2.50(2)
W(5)-O(16)	1.960(12)	W(10)-O(27)	2.070(12)	K(1)-O(47)	2.529(17)
W(5)-O(9)	2.165(12)	W(10)-O(22)	2.072(11)	K(1)-O(49)	2.592(19)

Symmetry transformations used to generate equivalent atoms: i: -x+1/2, -y+1/2, -z; ii: -x+1/2, y+1/2, -z+1/2; iii: -x+1/2, y-1/2, -z+1/2.

Table S10. Selected bond angles for **3**.

Bond angle	(°)	Bond angle	(°)
O(33)-W(1)-O(37)	98.9(6)	O(36)-W(8)-O(9)	73.9(4)
O(33)-W(1)-O(35)	100.2(6)	O(37)-W(8)-O(9)	73.0(5)
O(37)-W(1)-O(35)	160.8(5)	O(26)-W(9)-O(22)	101.5(6)
O(33)-W(1)-O(27)^{i}	101.8(6)	O(26)-W(9)-O(35)	101.9(6)
O(37)-W(1)-O(27)^{i}	89.4(5)	O(22)-W(9)-O(35)	88.5(5)
O(35)-W(1)-O(27)^{i}	86.9(5)	O(26)-W(9)-O(12)	96.1(6)
O(33)-W(1)-O(16)	95.3(6)	O(22)-W(9)-O(12)	88.8(5)
O(37)-W(1)-O(16)	90.0(5)	O(35)-W(9)-O(12)	162.0(5)
O(35)-W(1)-O(16)	88.0(5)	O(3)-W(8)-O(9)	166.2(6)
O(27)^{i}-W(1)-O(16)	162.8(5)	O(28)-W(8)-O(9)	88.4(5)
O(33)-W(1)-O(9)	167.6(6)	O(17)^{i}-W(8)-O(9)	87.3(5)
O(37)-W(1)-O(9)	74.9(5)	O(26)-W(9)-O(6)	95.2(6)
O(35)-W(1)-O(9)	86.2(5)	O(22)-W(9)-O(6)	163.2(5)
O(27)^{i}-W(1)-O(9)	89.0(5)	O(35)-W(9)-O(6)	89.1(5)
O(16)-W(1)-O(9)	74.2(5)	O(12)-W(9)-O(6)	88.3(5)
O(25)-W(2)-O(7)	97.3(6)	O(26)-W(9)-O(11)	165.5(6)
O(25)-W(2)-O(23)	100.8(6)	O(22)-W(9)-O(11)	89.0(5)
O(7)-W(2)-O(23)	95.8(5)	O(35)-W(9)-O(11)	88.2(5)
O(25)-W(2)-O(24)	99.9(6)	O(12)-W(9)-O(11)	73.9(5)
O(7)-W(2)-O(24)	161.4(5)	O(6)-W(9)-O(11)	74.3(5)
O(23)-W(2)-O(24)	87.8(5)	O(29)-W(10)-O(17)	95.4(6)
O(25)-W(2)-O(32)	99.4(6)	O(29)-W(10)-O(19)^{i}	166.4(5)
O(7)-W(2)-O(32)	87.7(5)	O(17)-W(10)-O(19)^{i}	95.1(5)
O(23)-W(2)-O(32)	158.9(5)	O(29)-W(10)-O(19)	93.5(5)
O(24)-W(2)-O(32)	82.6(5)	O(17)-W(10)-O(19)	168.0(5)
O(25)-W(2)-O(13)	169.9(5)	O(19)^{i}-W(10)-O(19)	77.4(5)
O(7)-W(2)-O(13)	75.0(5)	O(29)-W(10)-O(27)	94.7(5)
O(23)-W(2)-O(13)	74.0(5)	O(17)-W(10)-O(27)	91.6(5)
O(24)-W(2)-O(13)	88.6(5)	O(19)^{i}-W(10)-O(27)	93.5(5)
O(32)-W(2)-O(13)	86.9(5)	O(19)-W(10)-O(27)	79.7(4)
O(31)-W(3)-O(10)	104.6(6)	O(29)-W(10)-O(22)	90.6(5)
O(31)-W(3)-O(30)	100.0(6)	O(17)-W(10)-O(22)	95.8(5)
O(10)-W(3)-O(30)	94.2(6)	O(19)^{i}-W(10)-O(22)	79.8(5)
O(31)-W(3)-O(20)	95.3(6)	O(19)-W(10)-O(22)	92.1(5)
O(10)-W(3)-O(20)	91.4(5)	O(27)-W(10)-O(22)	170.4(5)
O(30)-W(3)-O(20)	161.8(5)	O(11)-Zn(1)-O(19)	112.5(5)
O(31)-W(3)-O(23)	92.3(6)	O(11)-Zn(1)-O(9)	107.0(5)
O(10)-W(3)-O(23)	162.9(5)	O(19)-Zn(1)-O(9)	113.5(5)
O(30)-W(3)-O(23)	85.4(5)	O(11)-Zn(1)-O(13)	107.6(5)
O(20)-W(3)-O(23)	84.1(5)	O(19)-Zn(1)-O(13)	108.0(5)
O(31)-W(3)-O(13)	162.5(6)	O(9)-Zn(1)-O(13)	108.1(5)
O(10)-W(3)-O(13)	89.9(5)	O(31)-Ni(1)-O(43)	91.3(6)
O(30)-W(3)-O(13)	88.5(5)	O(31)-Ni(1)-O(8)	87.1(8)
O(20)-W(3)-O(13)	74.2(5)	O(43)-Ni(1)-O(8)	178.3(9)

O(23)-W(3)-O(13)	73.0(5)	O(31)-Ni(1)-O(40)	176.9(8)
O(1)-W(4)-O(24)	102.9(6)	O(43)-Ni(1)-O(40)	91.1(8)
O(1)-W(4)-O(34)	100.0(7)	O(8)-Ni(1)-O(40)	90.6(9)
O(24)-W(4)-O(34)	86.5(6)	O(31)-Ni(1)-O(38)	88.4(7)
O(1)-W(4)-O(6)	96.6(6)	O(43)-Ni(1)-O(38)	93.2(8)
O(24)-W(4)-O(6)	160.0(5)	O(8)-Ni(1)-O(38)	87.1(10)
O(34)-W(4)-O(6)	85.9(6)	O(40)-Ni(1)-O(38)	89.4(9)
O(1)-W(4)-O(2)	97.0(6)	O(31)-Ni(1)-O(39)	93.1(7)
O(24)-W(4)-O(2)	91.0(5)	O(43)-Ni(1)-O(39)	89.1(8)
O(34)-W(4)-O(2)	162.9(5)	O(8)-Ni(1)-O(39)	90.6(10)
O(6)-W(4)-O(2)	90.9(5)	O(40)-Ni(1)-O(39)	89.0(10)
O(1)-W(4)-O(11)	166.7(6)	O(38)-Ni(1)-O(39)	177.1(8)
O(24)-W(4)-O(11)	87.9(5)	O(15)-Ni(2)-O(4)	88.1(6)
O(34)-W(4)-O(11)	88.3(5)	O(15)-Ni(2)-O(42)	91.8(6)
O(6)-W(4)-O(11)	73.4(4)	O(4)-Ni(2)-O(42)	178.7(8)
O(2)-W(4)-O(11)	74.8(5)	O(15)-Ni(2)-O(41)	90.4(6)
O(14)-W(5)-O(32)	103.0(6)	O(4)-Ni(2)-O(41)	88.8(8)
O(14)-W(5)-O(34)	100.4(6)	O(42)-Ni(2)-O(41)	92.5(8)
O(32)-W(5)-O(34)	87.4(6)	O(15)-Ni(2)-O(44)	177.0(6)
O(14)-W(5)-O(36)	95.3(6)	O(4)-Ni(2)-O(44)	89.2(6)
O(32)-W(5)-O(36)	89.8(5)	O(42)-Ni(2)-O(44)	90.9(6)
O(34)-W(5)-O(36)	164.3(5)	O(41)-Ni(2)-O(44)	90.8(7)
O(14)-W(5)-O(16)	96.0(5)	O(15)-Ni(2)-O(21)	90.5(6)
O(32)-W(5)-O(16)	161.0(5)	O(4)-Ni(2)-O(21)	89.0(7)
O(34)-W(5)-O(16)	87.9(5)	O(42)-Ni(2)-O(21)	89.7(8)
O(36)-W(5)-O(16)	89.8(5)	O(41)-Ni(2)-O(21)	177.6(8)
O(14)-W(5)-O(9)	165.8(5)	O(44)-Ni(2)-O(21)	88.2(7)
O(32)-W(5)-O(9)	87.2(5)	O(45)-V(1)-O(18)	93.7(6)
O(34)-W(5)-O(9)	89.8(5)	O(45)-V(1)-O(10)	95.5(6)
O(36)-W(5)-O(9)	74.6(5)	O(18)-V(1)-O(10)	89.2(5)
O(16)-W(5)-O(9)	74.4(5)	O(45)-V(1)-O(19)	173.2(6)
O(5)-W(6)-O(29)	100.4(7)	O(18)-V(1)-O(19)	89.9(5)
O(5)-W(6)-O(30)	99.8(6)	O(10)-V(1)-O(19)	90.3(5)
O(29)-W(6)-O(30)	90.2(6)	O(45)-V(1)-O(27)	98.5(6)
O(5)-W(6)-O(12)	99.5(6)	O(18)-V(1)-O(27)	167.6(5)
O(29)-W(6)-O(12)	86.0(5)	O(10)-V(1)-O(27)	91.9(5)
O(30)-W(6)-O(12)	160.7(5)	O(19)-V(1)-O(27)	77.8(5)
O(5)-W(6)-O(2)	97.7(6)	O(45)-V(1)-O(22)^{i}	96.7(6)
O(29)-W(6)-O(2)	161.6(5)	O(18)-V(1)-O(22)^{i}	91.8(5)
O(30)-W(6)-O(2)	89.7(6)	O(10)-V(1)-O(22)^{i}	167.7(5)
O(12)-W(6)-O(2)	88.0(5)	O(19)-V(1)-O(22)^{i}	77.4(5)
O(5)-W(6)-O(11)	170.2(6)	O(27)-V(1)-O(22)^{i}	84.5(5)
O(29)-W(6)-O(11)	86.3(5)	O(46)-K(1)-O(48)	141.5(7)
O(30)-W(6)-O(11)	87.3(5)	O(46)-K(1)-O(26)	140.3(6)
O(12)-W(6)-O(11)	73.7(5)	O(48)-K(1)-O(26)	72.8(5)
O(2)-W(6)-O(11)	75.3(5)	O(46)-K(1)-O(50)	75.9(7)
O(15)-W(7)-O(18)	104.5(6)	O(48)-K(1)-O(50)	107.3(7)
O(15)-W(7)-O(28)	99.5(6)	O(26)-K(1)-O(50)	73.4(6)

O(18)-W(7)-O(28)	92.3(5)	O(46)-K(1)-O(33)^{iii}	77.0(6)
O(15)-W(7)-O(20)	96.8(6)	O(48)-K(1)-O(33)^{iii}	78.2(6)
O(18)-W(7)-O(20)	93.1(5)	O(26)-K(1)-O(33)^{iii}	141.5(5)
O(28)-W(7)-O(20)	160.9(5)	O(50)-K(1)-O(33)^{iii}	140.7(6)
O(15)-W(7)-O(7)	92.9(5)	O(46)-K(1)-O(51)	75.5(7)
O(18)-W(7)-O(7)	162.6(5)	O(48)-K(1)-O(51)	142.7(6)
O(28)-W(7)-O(7)	85.3(5)	O(26)-K(1)-O(51)	76.0(6)
O(20)-W(7)-O(7)	84.1(5)	O(50)-K(1)-O(51)	82.4(7)
O(15)-W(7)-O(13)	163.7(5)	O(33)^{iii}-K(1)-O(51)	117.4(6)
O(18)-W(7)-O(13)	89.7(5)	O(46)-K(1)-O(47)	119.9(7)
O(28)-W(7)-O(13)	87.6(5)	O(48)-K(1)-O(47)	81.7(6)
O(20)-W(7)-O(13)	74.1(5)	O(26)-K(1)-O(47)	74.7(5)
O(7)-W(7)-O(13)	73.0(5)	O(50)-K(1)-O(47)	142.3(7)
O(3)-W(8)-O(28)	102.3(6)	O(33)^{iii}-K(1)-O(47)	76.6(5)
O(3)-W(8)-O(17)^{i}	101.1(7)	O(51)-K(1)-O(47)	70.7(7)
O(28)-W(8)-O(17)^{i}	91.5(6)	O(46)-K(1)-O(49)	76.2(7)
O(3)-W(8)-O(36)	96.7(6)	O(48)-K(1)-O(49)	69.0(6)
O(28)-W(8)-O(36)	91.7(5)	O(26)-K(1)-O(49)	116.4(6)
O(17)^{i}-W(8)-O(36)	160.8(5)	O(50)-K(1)-O(49)	72.1(7)
O(3)-W(8)-O(37)	96.7(6)	O(33)^{iii}-K(1)-O(49)	74.1(5)
O(28)-W(8)-O(37)	161.0(5)	O(51)-K(1)-O(49)	145.7(7)
O(17)^{i}-W(8)-O(37)	84.1(5)	O(47)-K(1)-O(49)	141.9(6)
O(36)-W(8)-O(37)	86.7(5)		

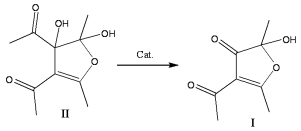
Symmetry transformations used to generate equivalent atoms: i: -x+1/2, -y+1/2, -z; ii: -x+1/2, y+1/2, -z+1/2; iii: -x+1/2, y-1/2, -z+1/2.

Table S11. Oxidative cyclization of acetylacetone catalyzed by various catalysts.[a]

Entry	Catalyst	**I**[b]	**II**[b]
1	$MnCl_2·4H_2O$	0	0
2	$CoCl_2·6H_2O$	0	0
3	$NiCl_2·6H_2O$	0	0
4	$Na_{12}\{Zn_5W_{19}\}$	0	0
5	$K_{12}\{V_2Zn_3W_{19}\}$	46	0
6	$K_{12}\{V_2Zn_3W_{19}\}$ + $MnCl_2$	44.8	0[c]
7	$K_{12}\{V_2Zn_3W_{19}\}$ + $CoCl_2$	40.3	0[c]
8	$K_{12}\{V_2Zn_3W_{19}\}$ + $NiCl_2$	46.6	0[c]

[a]Catalyst (0.01 mmol), acetylacetone (0.5 mmol) and H_2O_2 (1.0 mmol) were stirred in acetonitrile (0.8 mL) at 60 ^{o}C for 12 h. [b]Isolated yield (%). [c]The addictives are 0.04 mmol.

Table S12. Catalytic transformation from **II** to **I** catalyzed by various catalysts.[a]



Entry	Catalyst	Yield(%)[b]	Yield(%)[c]
1	-	0	0
2	$\{V_2Zn_3W_{19}\}$	10	100
3	**1**	20	100
4	**2**	10	80
5	**3**	10	80
6	$MnCl_2$	100	-[d]
7	$CoCl_2$	0	0[d]
8	$NiCl_2$	0	0[d]
9	$\{Zn_5W_{19}\}$	0	0

[a]Catalyst (0.01 mmol) and **II** (0.5 mmol) were stirred in acetonitrile (0.8 mL) at 60 °C for 12 h. [b]Without H_2O_2 under insert N_2 atmosphere. [c]In the presence of H_2O_2 (0.5 mmol). [d]Catalyst loading: 0.04 mmol.

Figures:

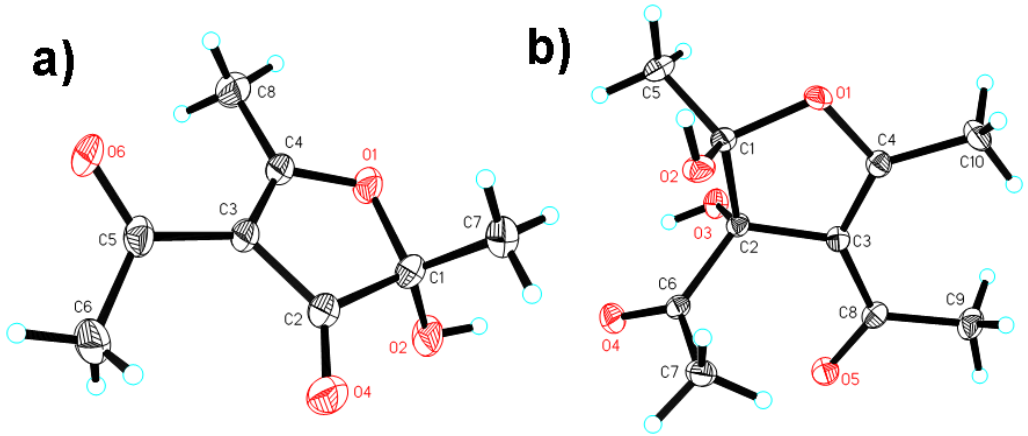


Fig. S1. ORTEP representations of the structures for **I** (a) and **II** (b). The ellipsoids are shown at 30% probability.

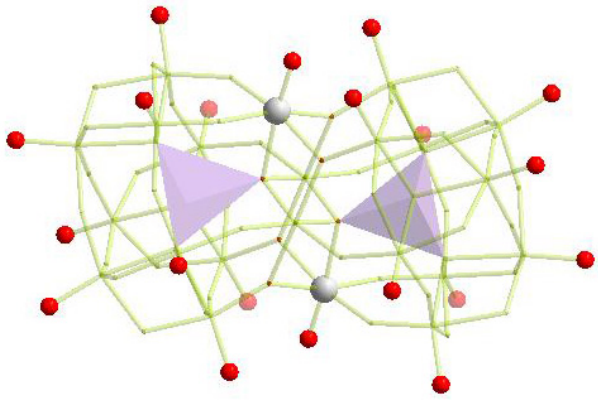


Fig. S2. Ball-and-stick and polyhedral representations of the polyoxoanion $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$ (O, red ball; V, gray ball; $\{ZnO_4\}$, lavender tetrahedron).

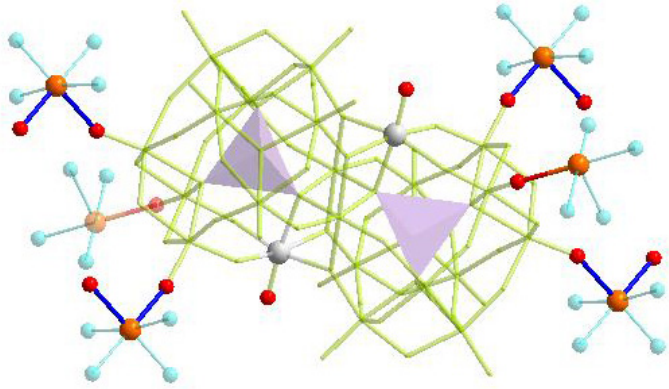


Fig. S3. A view of the polyoxoanion $\{[Mn_4(H_2O)_{18}][WZn(VO)_2(ZnW_9O_{34})_2]\}^{4-}$ in **1** (Orange balls represent manganese atoms).

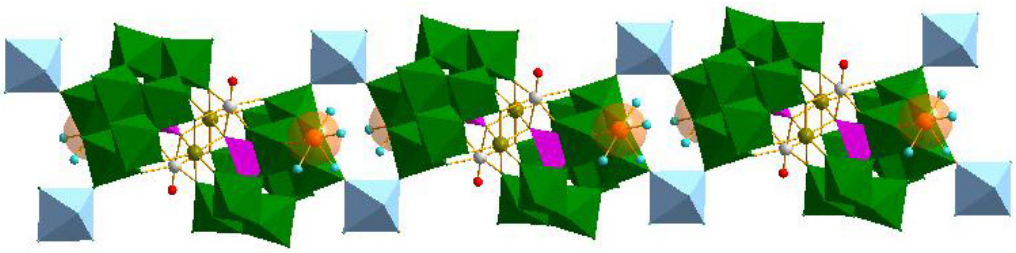


Fig. S4. The infinite 1D polymeric anion of Mn^{2+} ions (pale blue octahedra) linking up $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$.

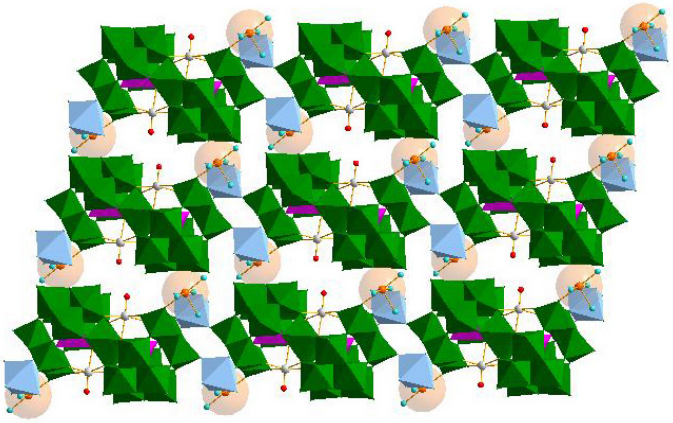


Fig. S5. The 3D supramolecular framework of **1** as viewed down the *b* axis.

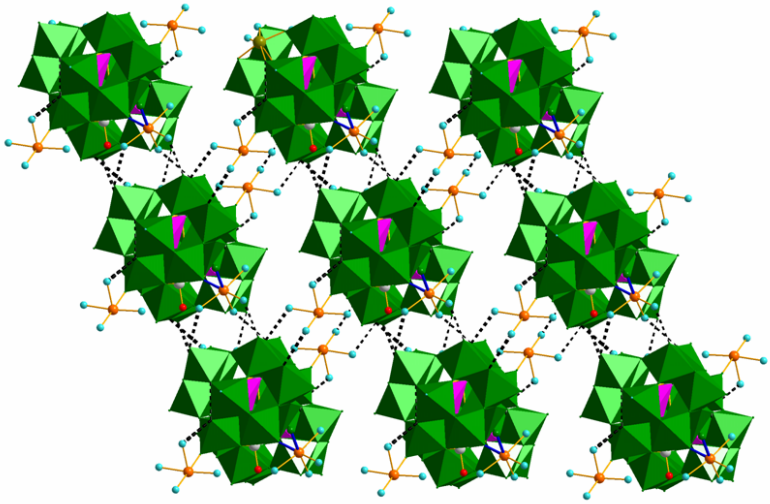


Fig. S6. Packing diagram of **1** as viewed down the *c* axis (the dashed lines represent hydrogen bonds).

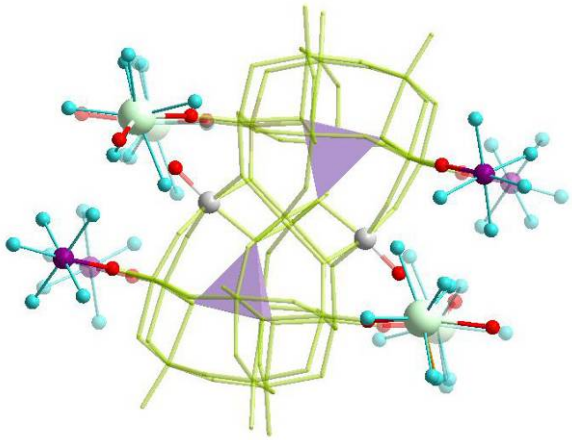


Fig. S7. A view of the coordination mode of $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$ in **2** (Light green balls represent potassium atoms; Violet balls represent cobalt atoms).

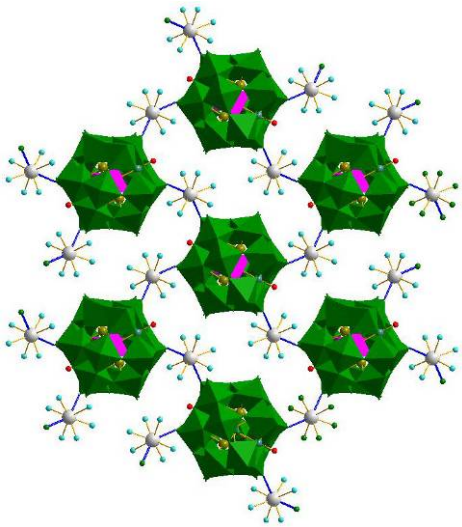


Fig. S8. A view of the lamellar network of the polyanion $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$ linked by potassium ions in **2**.

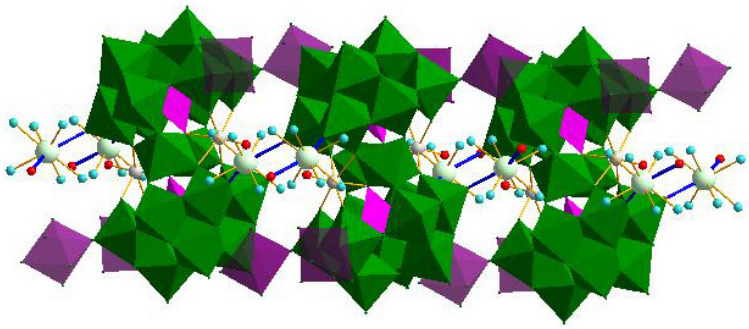


Fig. S9. Side view of the lamellar network in **2** as viewed down *b* axis (Violet octahedra represent cobalt ions).

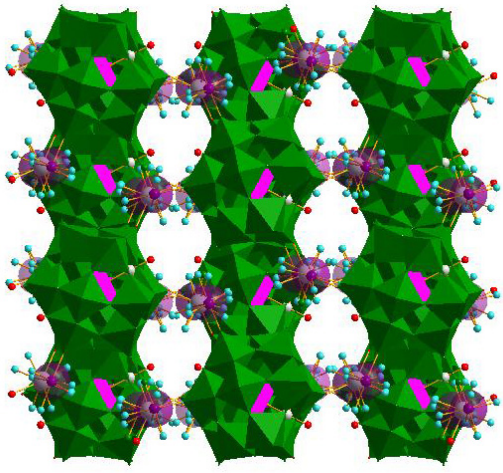


Fig. S10. The 3D supramolecular network of **2** as viewed down the *a* axis.

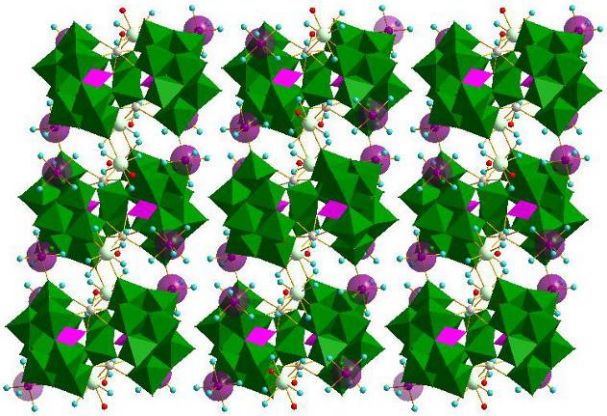


Fig. S11. The 3D supramolecular network of **2** as viewed down the *b* axis.

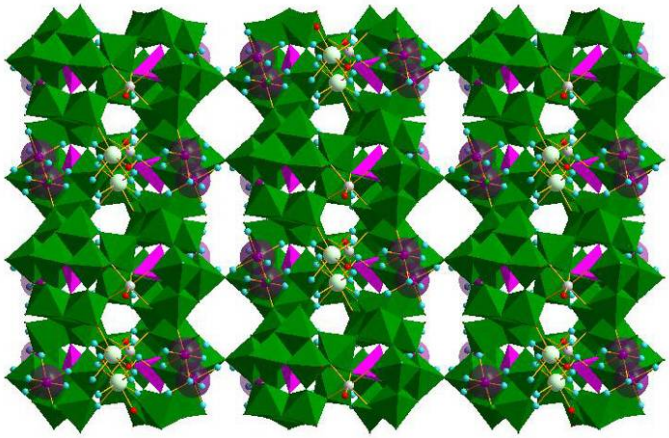


Fig. S12. The 3D supramolecular network of **2** as viewed down the *c* axis.

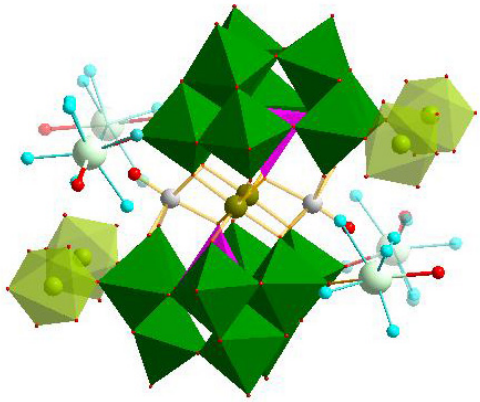


Fig. S13. Polyhedral and ball-and-stick representations of the polyoxoanion $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$ coordinated by potassium and cobalt cations in compound **3** (Light green balls represent potassium atoms; Lime octahedra represent nickel ions).

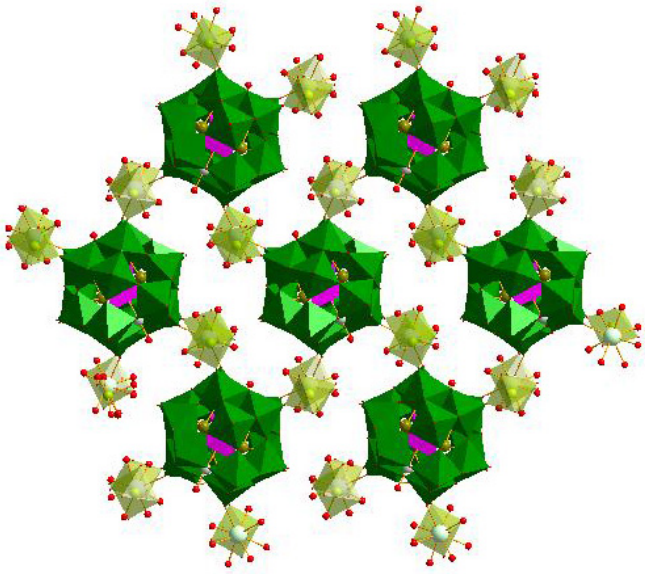


Fig. S14. A view of the lamellar network of $[\{Ni(H_2O)_5\}_4][WZn(VO)_2(ZnW_9O_{34})_2]$ linked by K^+ cations in **3**.

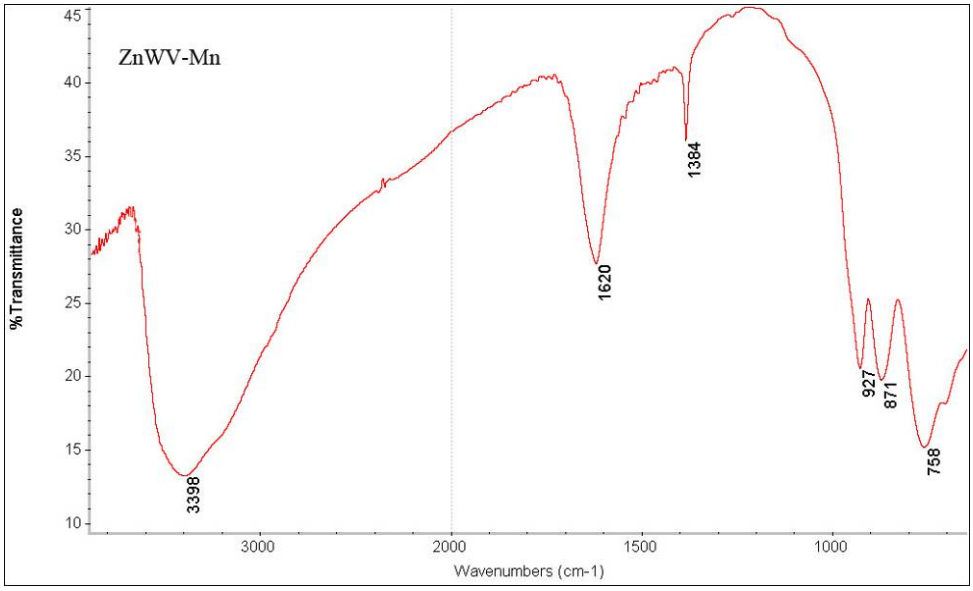


Fig. S15. IR spectrum of compound **1**.

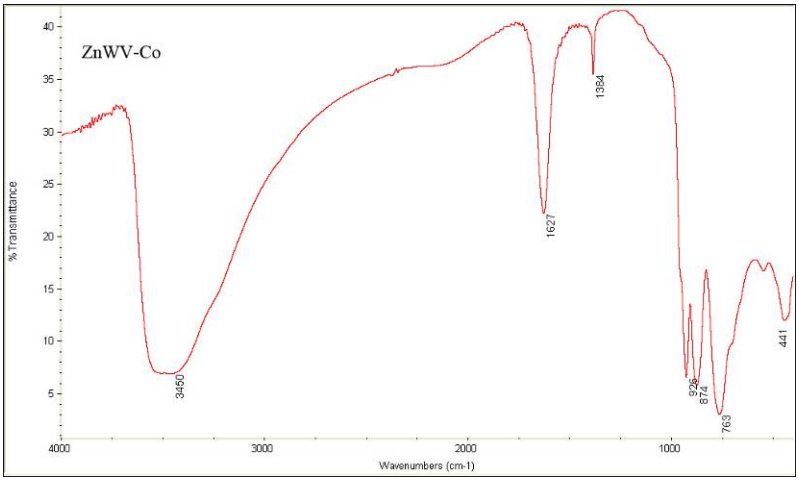


Fig. S16. IR spectrum of compound **2**.

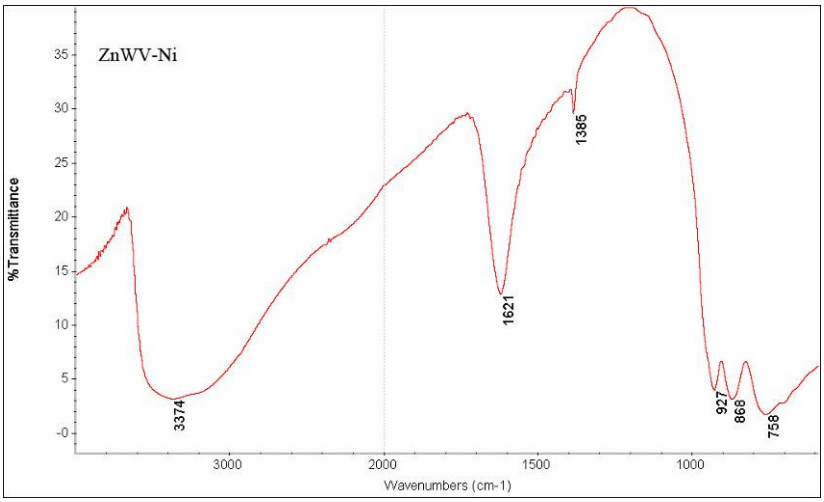


Fig. S17. IR spectrum of compound **3**.

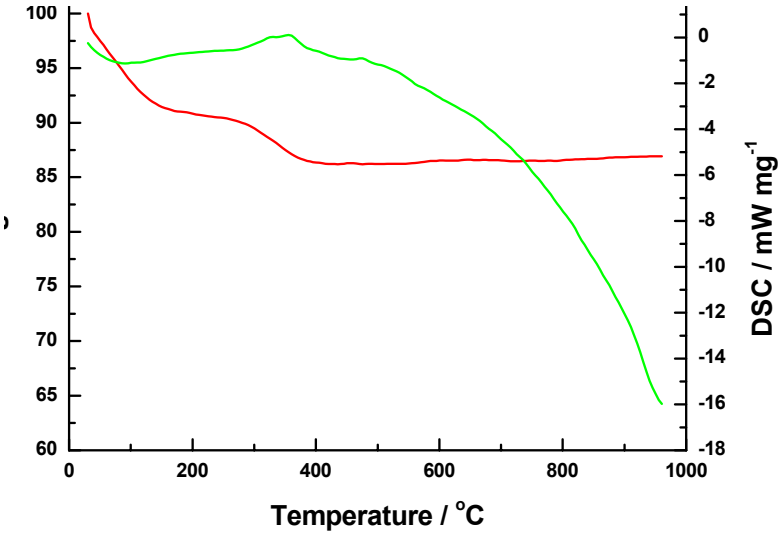


Fig. S18. TGA results of **1**.

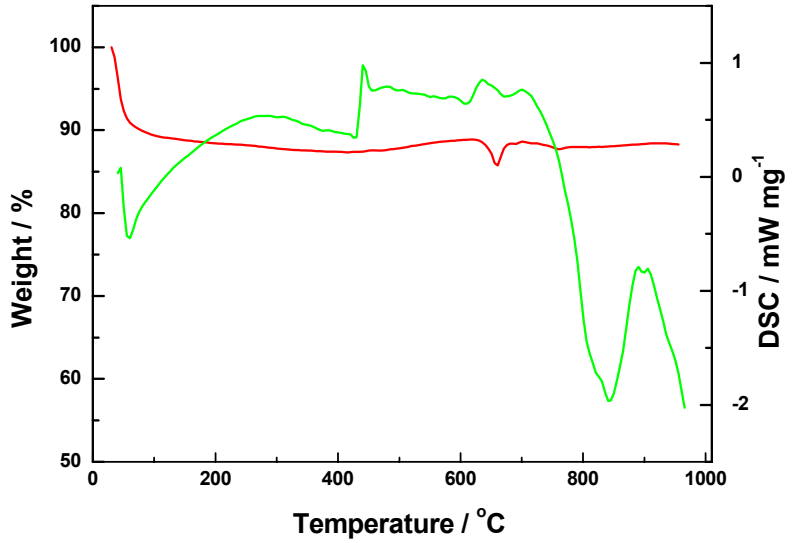


Fig. S19. TGA results of **2**.

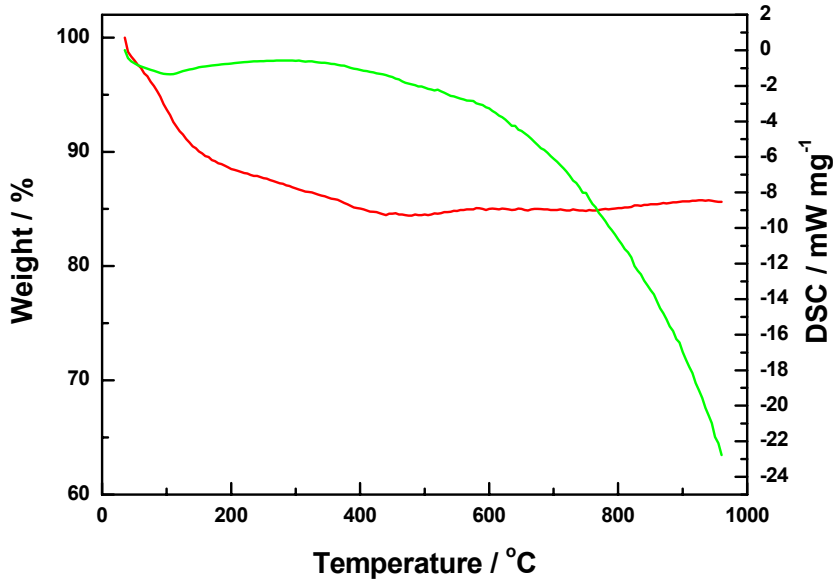


Fig. S20. TGA results of **3**.

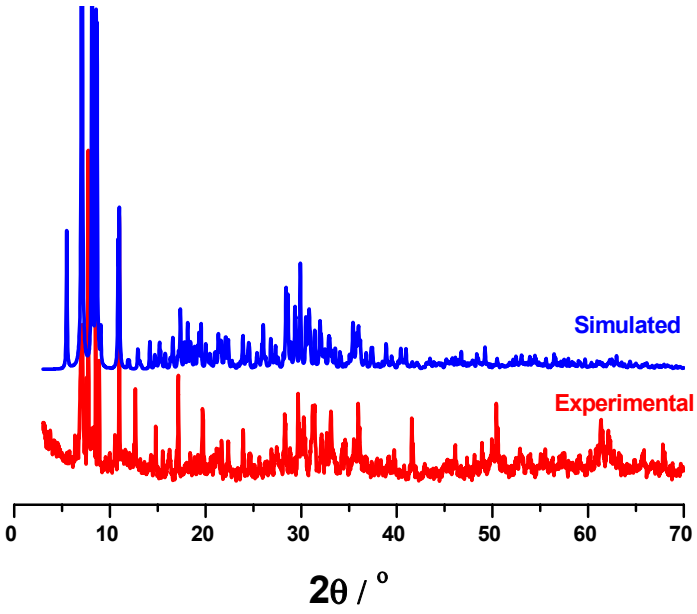


Fig. S21. Powder X-ray diffraction patterns for compound **1**.

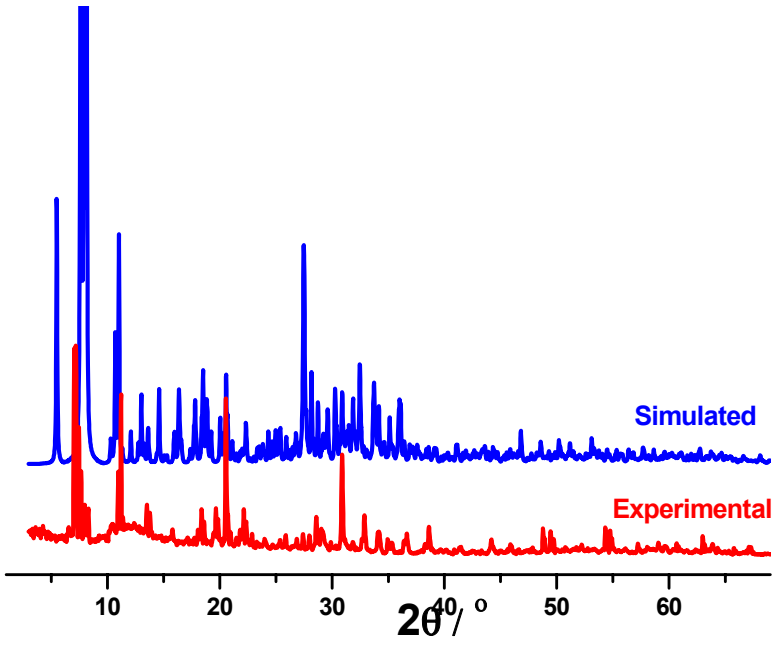


Fig. S22. Powder X-ray diffraction patterns for compound **2**.

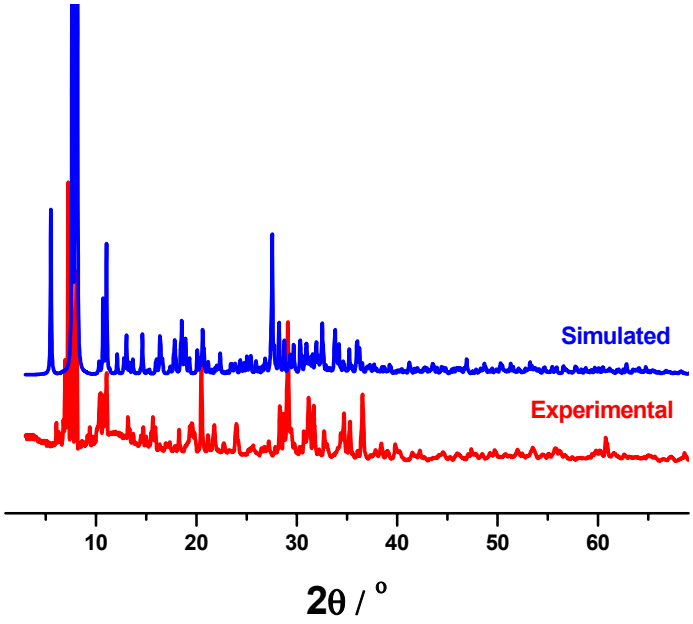


Fig. S23. Powder X-ray diffraction patterns for compound **3**.