

Table S1. Summary of X-ray Crystallographic Data for
 $(\text{NH}_4)_9\text{K}[\text{Co}^{2+}\text{W}_{11}\text{O}_{35}(\text{O}_2)_4]\cdot 5\text{H}_2\text{O}$.

empirical formula	$\text{W}_{11}\text{CoO}_{48}\text{KN}_9\text{H}_{46}$
fw	3060.78
crystal colour and shape	blue multi-faceted prism
crystal system	monoclinic
space group	$\text{P}2_1/\text{m}$
a (Å)	10.8607(2)
b (Å)	17.437(3)
c (Å)	16.268(3)
β (deg)	123.32(2)
V (Å ³)	2514.0(2)
Z	2
density (calcd)	4.04 g/cm ³ (4.16)
crystal size (mm)	0.20x0.15x0.10
radiation	$\text{MoK}\alpha$ ($\lambda=0.7107$ Å)
temperature (K)	293(2)
absn coeff μ (cm ⁻¹)	261.2
trans coeff (mean)	0.413-0.997 (0.758)
range θ collected (deg)	1-21
intensity measurement method	$\theta/2\theta$
no. of reflns colld	2404
no. of obsd reflns	1824 ($I>10\sigma_I$)
parameters refined	181
goodness-of-fit on F^2	1.21
R^a	0.042
R_w^a	0.058
max peak in diff map (e/Å ³)	1.69

$$^a R = \Sigma(F_o - F_c) / \Sigma(F_o), R_w = [\Sigma[w(F_o - F_c)^2] / \Sigma[w(F_o)^2]]^{1/2}$$

Table S2. Atomic Coordinates and Thermal Parameters in
(NH₄)₉K[Co²⁺W₁₁O₃₅(O₂)₄]·5H₂O.

Atom	x	y	z	B/B _{eq}
Co	-0.0180(5)	0.250	-0.2225(3)	0.8(1)
W(1)	0.0550(1)	0.3414(1)	-0.3844(1)	1.45(3)*
W(2)	-0.3400(1)	0.3573(1)	-0.4191(1)	1.65(3)*
W(3)	-0.0531(1)	0.4399(1)	-0.2292(1)	1.61(3)*
W(4)	-0.3069(1)	0.3552(1)	-0.2056(1)	1.26(3)*
W(5)	0.2663(1)	0.3430(1)	-0.0034(1)	1.60(3)*
W(6)	0.0040(2)	0.250	0.0167(1)	1.61(5)*
O(1)	0.246(2)	0.349(1)	-0.329(1)	2.8(5)
O(2)	-0.487(2)	0.395(1)	-0.531(1)	3.1(5)
O(3)	-0.004(2)	0.541(1)	-0.210(1)	3.3(5)
O(4)	-0.424(2)	0.389(1)	-0.172(1)	1.7(4)
O(5)	0.344(2)	0.345(1)	-0.075(1)	2.6(5)
O(6)	-0.056(3)	0.250	0.098(2)	3.1(7)
O(11)	0.026(3)	0.250	-0.463(2)	2.1(6)
O(12)	-0.188(2)	0.324(1)	-0.445(1)	2.2(4)
O(13)	0.059(2)	0.397(1)	-0.271(1)	2.6(5)
O(18)	-0.003(2)	0.445(1)	-0.440(1)	3.4(5)
O(19)	-0.001(2)	0.390(1)	-0.503(1)	3.0(5)
O(22)	-0.386(2)	0.250	-0.435(1)	0.5(5)
O(23)	-0.230(2)	0.453(1)	-0.366(1)	1.4(4)
O(24)	-0.438(2)	0.374(1)	-0.348(1)	1.9(4)
O(34)	-0.204(2)	0.452(1)	-0.193(1)	2.4(5)
O(35)	0.084(2)	0.403(1)	-0.104(1)	2.0(4)
O(44)	-0.374(2)	0.250	-0.236(1)	0.1(5)
O(46)	-0.141(2)	0.323(1)	-0.087(1)	1.2(4)
O(55)	0.379(3)	0.250	0.076(2)	1.1(5)
O(56)	0.146(2)	0.334(1)	0.065(1)	2.3(4)
O(58)	0.318(2)	0.446(1)	0.054(1)	3.4(5)
O(59)	0.428(3)	0.389(2)	0.118(2)	5.2(6)
O(110)	0.066(3)	0.250	-0.303(2)	1.0(5)
O(234)	-0.165(2)	0.333(1)	-0.265(1)	0.6(4)
O(556)	0.125(2)	0.250	-0.079(1)	0.3(5)
K	0.413(1)	0.250	0.826(1)	4.2(3)
O(101)	0.286(3)	0.598(2)	0.951(2)	5.1(7)
O(102)	0.297(5)	0.588(3)	0.661(3)	13(2)
O(104)	0.18(1)	0.750	0.665(7)	9(3)
N(1)	0.290(5)	0.250	0.517(3)	5(1)
N(2)	0.514(6)	0.250	0.271(3)	7(1)
N(3)	0.277(4)	0.460(2)	0.527(2)	6.1(9)
N(4)	0.351(4)	0.495(2)	0.826(3)	8(1)
N(5)	0.331(4)	0.406(3)	0.257(3)	8(1)
N(6)	0.000	0.500	0.000	12(2)

*Starred atoms were anisotropically refined. $B_{eq} = 8\pi^2/3 \cdot \Sigma [U_{ij} \cdot a_i \cdot a_j \cdot \cos(a_i, a_j)]$

U_{ij}

Table S3. Anisotropic Thermal Parameters for Tungsten Atoms in
(NH₄)₉K[Co²⁺W₁₁O₃₅(O₂)₄]·5H₂O as $\exp[-2\pi^2 \cdot \sum(U_{ij} \cdot a_i^* \cdot a_j^* \cdot h_i \cdot h_j) \cdot 10^3]$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
W(1)	13.6(5)	20.4(7)	24.8(5)	1.1(5)	12.8(3)	6.4(5)
W(2)	18.6(5)	14.7(7)	20.4(5)	4.7(5)	6.9(4)	7.8(5)
W(3)	15.9(5)	8.5(7)	38.5(6)	-3.5(5)	16.0(4)	-3.5(5)
W(4)	11.4(5)	14.0(8)	24.2(5)	1.4(5)	10.8(3)	-0.4(5)
W(5)	13.1(5)	25.7(8)	21.1(5)	-5.4(5)	8.9(3)	-8.8(5)
W(6)	14.3(8)	38(1)	11.3(7)	0	8.6(5)	0

Table S4 Bond Distances in the $[\text{Co}^{2+}\text{W}_{11}\text{O}_{35}(\text{O}_2)_4]^{10-}$ anion.

W(1)–O(1)	1.71(1)	W(4)–O(34)	1.96(1)
W(1)–O(11)	1.96(1)	W(4)–O(44)	1.93(1)
W(1)–O(12)	2.21(1)	W(4)–O(46)	1.84(1)
W(1)–O(13)	2.06(1)	W(4)–O(234)	2.23(1)
W(1)–O(18)	1.96(1)	W(4)–O(4)	1.71(1)
W(1)–O(19)	1.89(1)	W(4)–O(24)	1.96(1)
W(1)–O(110)	2.03(1)	W(5)–O(5)	1.76(1)
W(2)–O(2)	1.75(1)	W(5)–O(35)	2.01(1)
W(2)–O(12)	1.97(1)	W(5)–O(55)	2.01(1)
W(2)–O(22)	1.92(1)	W(5)–O(56)	2.12(1)
W(2)–O(23)	1.94(1)	W(5)–O(58)	1.95(1)
W(2)–O(24)	1.96(1)	W(5)–O(59)	1.94(2)
W(2)–O(234)	2.19(1)	W(5)–O(556)	2.09(1)
W(3)–O(3)	1.82(1)	W(6)–O(6)	1.75(2)
W(3)–O(13)	1.83(1)	W(6)–O(46)	2.00(1)
W(3)–O(23)	1.98(1)	W(6)–O(56)	1.93(1)
W(3)–O(34)	1.99(1)	W(6)–O(556)	2.51(1)
W(3)–O(35)	1.85(1)	Co–O(110)	1.95(2)
W(3)–O(234)	2.11(1)	Co–O(234)	1.95(1)
O(18)–O(19)	1.41(2)	Co–O(556)	1.96(2)
O(58)–O(59)	1.44(2)		

Table S5 Bond Angles in the $[\text{Co}^{2+}\text{W}_{11}\text{O}_{35}(\text{O}_2)_4]^{10-}$ anion.

O(11)–W(1)–O(1)	97.3(7)	O(24)–W(4)–O(4)	98.7(6)
O(11)–W(1)–O(13)	152.1(6)	O(24)–W(4)–O(34)	88.4(5)
O(12)–W(1)–O(1)	174.9(5)	O(24)–W(4)–O(44)	86.1(6)
O(12)–W(1)–O(11)	82.6(7)	O(24)–W(4)–O(46)	159.2(5)
O(12)–W(1)–O(13)	84.8(5)	O(34)–W(4)–O(4)	97.9(6)
O(13)–W(1)–O(1)	93.1(6)	O(44)–W(4)–O(4)	100.0(6)
O(18)–W(1)–O(1)	98.5(6)	O(44)–W(4)–O(34)	161.9(6)
O(18)–W(1)–O(11)	123.4(6)	O(46)–W(4)–O(4)	102.1(6)
O(18)–W(1)–O(12)	85.8(6)	O(46)–W(4)–O(34)	89.7(6)
O(18)–W(1)–O(13)	80.2(6)	O(46)–W(4)–O(44)	89.2(6)
O(19)–W(1)–O(1)	96.8(6)	O(234)–W(4)–O(4)	168.9(5)
O(19)–W(1)–O(11)	81.4(6)	O(234)–W(4)–O(24)	74.2(5)
O(19)–W(1)–O(12)	88.3(6)	O(234)–W(4)–O(34)	73.8(5)
O(19)–W(1)–O(13)	123.1(6)	O(234)–W(4)–O(44)	88.1(5)
O(19)–W(1)–O(18)	42.9(6)	O(234)–W(4)–O(46)	85.3(5)
O(110)–W(1)–O(1)	95.2(7)	O(5)–W(5)–O(35)	92.2(6)
O(110)–W(1)–O(11)	73.6(6)	O(5)–W(5)–O(58)	100.4(6)
O(110)–W(1)–O(12)	79.8(6)	O(35)–W(5)–O(58)	78.7(6)
O(110)–W(1)–O(13)	79.7(5)	O(55)–W(5)–O(5)	96.6(6)
O(110)–W(1)–O(18)	156.1(6)	O(55)–W(5)–O(35)	155.7(6)
O(110)–W(1)–O(19)	153.5(6)	O(55)–W(5)–O(56)	85.3(6)
O(2)–W(2)–O(12)	104.5(6)	O(55)–W(5)–O(58)	121.4(6)
O(2)–W(2)–O(22)	102.1(7)	O(55)–W(5)–O(59)	78.5(7)
O(2)–W(2)–O(23)	96.7(6)	O(55)–W(5)–O(556)	74.6(5)
O(12)–W(2)–O(22)	82.2(6)	O(56)–W(5)–O(5)	172.0(6)
O(23)–W(2)–O(12)	89.3(5)	O(56)–W(5)–O(35)	83.1(5)
O(23)–W(2)–O(22)	160.8(6)	O(56)–W(5)–O(58)	85.1(6)
O(24)–W(2)–O(2)	95.9(6)	O(59)–W(5)–O(5)	100.9(7)
O(24)–W(2)–O(12)	159.6(5)	O(59)–W(5)–O(35)	121.9(7)
O(24)–W(2)–O(22)	92.6(6)	O(59)–W(5)–O(56)	87.0(6)
O(24)–W(2)–O(23)	89.4(5)	O(59)–W(5)–O(58)	43.4(7)
O(234)–W(2)–O(2)	167.2(6)	O(59)–W(5)–O(556)	150.5(6)
O(234)–W(2)–O(12)	84.7(5)	O(556)–W(5)–O(5)	94.1(6)
O(234)–W(2)–O(22)	87.7(6)	O(556)–W(5)–O(35)	82.3(5)
O(234)–W(2)–O(23)	74.3(5)	O(556)–W(5)–O(56)	78.9(5)
O(234)–W(2)–O(24)	75.3(5)	O(556)–W(5)–O(58)	156.4(6)
O(13)–W(3)–O(3)	106.3(6)	O(6)–W(6)–O(46)	102.0(6)
O(13)–W(3)–O(34)	160.8(6)	O(6)–W(6)–O(56)	102.4(6)
O(13)–W(3)–O(35)	89.4(6)	O(6)–W(6)–O(556)	172.2(8)
O(23)–W(3)–O(3)	95.2(6)	O(46)–W(6)–O(46)	79.3(7)
O(23)–W(3)–O(13)	92.3(5)	O(46)–W(6)–O(56)	85.8(5)
O(23)–W(3)–O(34)	84.0(5)	O(46)–W(6)–O(56)	153.6(5)
O(23)–W(3)–O(35)	164.0(5)	O(46)–W(6)–O(56)	85.8(5)
O(34)–W(3)–O(3)	92.8(6)	O(46)–W(6)–O(556)	84.0(4)
O(35)–W(3)–O(3)	99.6(6)	O(56)–W(6)–O(56)	98.7(8)
O(35)–W(3)–O(34)	89.2(6)	O(556)–W(6)–O(56)	72.8(4)
O(234)–W(3)–O(3)	165.8(6)	O(110)–Co–O(556)	117.3(7)
O(234)–W(3)–O(13)	85.0(5)	O(234)–Co–O(110)	109.3(5)
O(234)–W(3)–O(23)	75.4(5)	O(234)–Co–O(234)	95.8(7)
O(234)–W(3)–O(34)	75.8(5)	O(234)–Co–O(556)	111.5(4)
O(234)–W(3)–O(35)	88.9(5)		

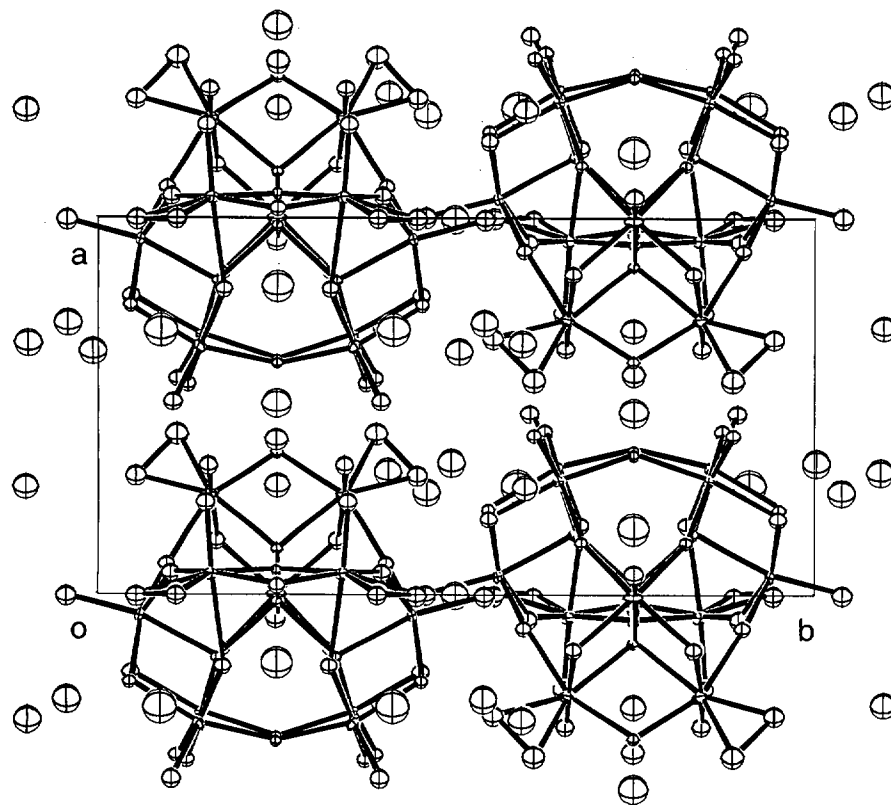


Figure S1. ORTEP diagram of the unit cell of $(\text{NH}_4)_9\text{K}[\text{Co}^{2+}\text{W}_{11}\text{O}_{35}(\text{O}_2)_4] \times 5\text{H}_2\text{O}$ viewed down the c axis.