Supporting Information

Two mixed-addenda Nb/W polyoxometalates-basedhybrid compounds containing multicopper units: synthesis, structures, electrochemical and magnetic properties

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Materials and Methods

$K_7HNb_6O_{19}$, $Na_9[A\text{-}PW_9O_{34}]$ were synthesized according to the literature.[1] All other chemical reagents were commercially available and used without further purification.

Elemental analyses were performed on an inductively coupled plasma (ICP) IRIS Intrepid atomic-emission spectrometer (Cu, P, W and Nb) and a Vario EL Elemental Analyzer (C, H, and N). FT-IR spectra were recorded in the range of 4000-400 cm^{-1} using KBr pellets with a Nicolet iS10 spectrometer. TG-DTA analyses were performed on a TA SDTQ600 thermal analyzer. Crystal data for compounds **1** and **2** were collected on a Bruker SMART APEXII single crystal diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The linear adsorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Empirical adsorption was applied. The structures were solved by the direct method and refined by full-matrix least-squares method on F^2 using *SHELXTL*-2017/1 crystallographic software package.[2] In the final refinement of crystal structures, most of the heavy metal atoms (P, W, Nb and Cu) were refined anisotropically, and some of the light atoms (C, N and O) were refined isotropically. H atoms on the ligand were added theoretically on calculated positions. The selected bond lengths and angles are listed in Tables S1 and S2. X-ray powder diffraction patterns were performed on a Bruker D8 ADVANCE diffractometer with Cu-K_α radiation (λ = 1.5418 Å). Electrochemical measurements were performed on a CHI821C electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A

three-electrode system was employed with carbon paste electrode (CPE) as a working electrode, Ag/AgCl electrode as a reference electrode, Pt as a counter electrode. CPEs of **1** and **2** were prepared according to the literature.[3] Magnetic measurements were performed on a Superconducting Quantum Interference Design based-Vibrating Sample Magnetometer (SQUID-VSM) under the magnetic field of 1000 Oe.

The Hamilton given in the main text is

$$\hat{H}_{\mathrm{iso}} = -J\left(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3\right) - j\hat{S}_2\hat{S}_3 = -J\left(\hat{S}_T^2 - \sum_{i=1}^{3}\hat{S}_i^2\right)/2 + (J-j)(\hat{S}_{23}^2 - \hat{S}_2^2 - \hat{S}_3^2)$$

where

$$\hat{S}_T = \sum_{i=1}^{3}\hat{S}_i\,,\ \hat{S}_{23} = \hat{S}_2 + \hat{S}_3$$

The eigenvalue of $\hat{S}^2$ is $S(S+1)$, so the eigenvalue of this Hamiltonian is:

$$E(S_T,S_{23}) = -J\left[S_T(S_T+1) - \sum_{i=1}^{3}S_i(S_i+1)\right] + (J-j)[S_{23}(S_{23}+1) - S_2(S_2+1) - S_3(S_3+1)]$$

For a tricopper(II) unit, $S_{23} = 0$; 1, corresponding $S_T = 1/2$; 1/2, 3/2, the ground state energy level is $E(1/2, 0) = 3j/4$, $E(1/2, 1) = J - j/4$, $E(3/2,1) = -J/2 - j/4$, then substitute into van Vleck formula:

$$\chi_{\mathrm{M}} = \frac{N\beta^2 g^2}{3kT} \times \frac{\sum_{S_T} S_T(S_T+1)(2S_T+1)\exp(-E(S_T)/kT)}{\sum_{S_T}(2S_T+1)\exp(-E(S_T)/kT)} = \frac{N\beta^2 g^2}{4kT} \times \frac{1 + \exp((j-J)/kT) + 10\exp((2j+J)/2kT)}{1 + \exp((j-J)/kT) + 2\exp((2j+J)/2kT)}$$

which equals eq 3 in the main text.

which equals eq 3 in the main text.

Table S1 Selected bond lengths (Å) and bond angles (°) of **1**

P(1)-O(8)#1	1.534(10)	O(3)-W(3)-O(8)#3	83.6(4)
P(1)-O(8)#2	1.534(10)	O(6)#3-W(3)-O(8)#3	74.1(4)
P(1)-O(8)#3	1.534(10)	O(9)#3-W(3)-O(8)#3	74.3(4)
P(1)-O(8)	1.534(10)	O(7)#1-W(3)-O(8)#3	82.0(4)
W(1)-O(4)	1.691(11)	O(2)-Cu(1)-O(1)	177.1(4)
W(1)-O(10)	1.903(9)	O(2)-Cu(1)-N(2)	92.8(5)
W(1)-O(3)	1.919(10)	O(1)-Cu(1)-N(2)	88.9(5)
W(1)-O(9)	1.938(10)	O(2)-Cu(1)-N(4)	90.5(5)
W(1)-O(5)	1.946(10)	O(1)-Cu(1)-N(4)	87.9(6)
W(1)-O(8)	2.486(10)	N(2)-Cu(1)-N(4)	176.2(5)
W(2)-O(11)	1.739(10)	O(2)-Cu(1)-O(12)	80.0(5)
W(2)-O(7)	1.888(10)	O(1)-Cu(1)-O(12)	97.6(4)
W(2)-O(6)	1.932(10)	N(2)-Cu(1)-O(12)	92.1(5)
W(2)-O(5)	1.933(10)	N(4)-Cu(1)-O(12)	90.4(5)
W(2)-O(10)#3	1.943(10)	O(2)-Cu(1)-O(13)	91.0(7)
W(2)-O(8)	2.482(10)	O(1)-Cu(1)-O(13)	91.5(5)
W(3)-O(2)	1.788(11)	N(2)-Cu(1)-O(13)	83.2(6)
W(3)-O(3)	1.934(10)	N(4)-Cu(1)-O(13)	94.8(6)
W(3)-O(6)#3	1.954(11)	O(12)-Cu(1)-O(13)	169.6(7)
W(3)-O(9)#3	1.962(10)	N(5)#4-Cu(2)-N(1)	93.6(4)
W(3)-O(7)#1	1.973(10)	N(5)#4-Cu(2)-N(1)#5	93.6(4)
W(3)-O(8)#3	2.426(10)	N(1)-Cu(2)-N(1)#5	172.7(7)
Cu(1)-O(2)	1.956(11)	N(5)#4-Cu(2)-O(1)	180
Cu(1)-O(1)	1.968(8)	N(1)-Cu(2)-O(1)	86.4(4)
Cu(1)-N(2)	1.976(13)	N(1)#5-Cu(2)-O(1)	86.4(4)
Cu(1)-N(4)	1.996(13)	N(5)#4-Cu(2)-O(11)#6	90.6(3)
Cu(1)-O(12)	2.585(14)	N(1)-Cu(2)-O(11)#6	83.5(5)
Cu(1)-O(13)	2.598(18)	N(1)#5-Cu(2)-O(11)#6	96.5(5)
Cu(2)-N(5)#4	1.982(17)	O(1)-Cu(2)-O(11)#6	89.4(3)
Cu(2)-N(1)	2.021(12)	N(5)#4-Cu(2)-O(11)#7	90.6(3)
Cu(2)-N(1)#5	2.021(12)	N(1)-Cu(2)-O(11)#7	96.5(5)
Cu(2)-O(1)	2.032(16)	N(1)#5-Cu(2)-O(11)#7	83.5(5)
Cu(2)-O(11)#6	2.401(10)	O(1)-Cu(2)-O(11)#7	89.4(3)
Cu(2)-O(11)#7	2.401(10)	O(11)#6-Cu(2)-O(11)#7	178.9(6)
Cu(3)-Cu(3)#8	0.700(8)	Cu(3)#8-Cu(3)-N(3)	85.6(10)
Cu(3)-N(3)	1.963(16)	Cu(3)#8-Cu(3)-O(15)	112.6(14)
Cu(3)-O(15)	2.01(3)	N(3)-Cu(3)-O(15)	88.7(10)
Cu(3)-N(3)#8	2.033(17)	Cu(3)#8-Cu(3)-N(3)#8	74.3(9)
Cu(3)-O(14)#8	2.04(3)	N(3)-Cu(3)-N(3)#8	94.1(10)
Cu(3)-O(14)	2.36(3)	O(15)-Cu(3)-N(3)#8	172.7(12)
Cu(3)-O(15)#8	2.37(3)	Cu(3)#8-Cu(3)-O(14)#8	108.8(13)
C(1)-N(1)	1.32(2)	N(3)-Cu(3)-O(14)#8	165.4(11)

C(1)-N(3)	1.33(2)	O(15)-Cu(3)-O(14)#8	88.3(12)
C(2)-N(2)	1.28(2)	N(3)#8-Cu(3)-O(14)#8	87.3(10)
C(2)-N(3)	1.35(2)	Cu(3)#8-Cu(3)-O(14)	54.9(11)
C(3)-N(4)	1.25(2)	N(3)-Cu(3)-O(14)	80.6(9)
C(3)-N(5)	1.381(19)	O(15)-Cu(3)-O(14)	57.9(13)
N(1)-N(2)	1.324(18)	N(3)#8-Cu(3)-O(14)	129.2(10)
N(4)-N(4)#5	1.35(2)	O(14)#8-Cu(3)-O(14)	109.7(17)
O(13)-O(13')	0.84(10)	Cu(3)#8-Cu(3)-O(15)#8	51.5(12)
O(8)#1-P(1)-O(8)#2	109.6(4)	N(3)-Cu(3)-O(15)#8	137.1(11)
O(8)#1-P(1)-O(8)#3	109.1(7)	O(15)-Cu(3)-O(15)#8	104.5(16)
O(8)#2-P(1)-O(8)#3	109.6(4)	N(3)#8-Cu(3)-O(15)#8	77.9(9)
O(8)#1-P(1)-O(8)	109.6(4)	O(14)#8-Cu(3)-O(15)#8	57.4(13)
O(8)#2-P(1)-O(8)	109.1(7)	O(14)-Cu(3)-O(15)#8	73.2(10)
O(8)#3-P(1)-O(8)	109.6(4)	N(1)-C(1)-N(3)	111.4(15)
O(4)-W(1)-O(10)	104.1(5)	N(2)-C(2)-N(3)	114.2(16)
O(4)-W(1)-O(3)	100.4(5)	N(4)-C(3)-N(5)	114.6(15)
O(10)-W(1)-O(3)	86.5(4)	C(1)-N(1)-N(2)	107.2(12)
O(4)-W(1)-O(9)	101.2(5)	C(1)-N(1)-Cu(2)	128.5(11)
O(10)-W(1)-O(9)	88.7(4)	N(2)-N(1)-Cu(2)	121.2(9)
O(3)-W(1)-O(9)	158.4(4)	C(2)-N(2)-N(1)	105.9(13)
O(4)-W(1)-O(5)	102.3(5)	C(2)-N(2)-Cu(1)	132.4(11)
O(10)-W(1)-O(5)	153.6(4)	N(1)-N(2)-Cu(1)	121.6(10)
O(3)-W(1)-O(5)	87.9(4)	C(1)-N(3)-C(2)	101.0(15)
O(9)-W(1)-O(5)	87.0(4)	C(1)-N(3)-Cu(3)	136.2(14)
O(4)-W(1)-O(8)	172.3(5)	C(2)-N(3)-Cu(3)	121.4(13)
O(10)-W(1)-O(8)	81.3(4)	C(1)-N(3)-Cu(3)#8	117.1(13)
O(3)-W(1)-O(8)	85.3(4)	C(2)-N(3)-Cu(3)#8	136.1(13)
O(9)-W(1)-O(8)	73.2(4)	Cu(3)-N(3)-Cu(3)#8	20.1(3)
O(5)-W(1)-O(8)	72.5(4)	C(3)-N(4)-N(4)#5	106.8(9)
O(11)-W(2)-O(7)	103.2(5)	C(3)-N(4)-Cu(1)	131.9(11)
O(11)-W(2)-O(6)	99.9(5)	N(4)#5-N(4)-Cu(1)	121.3(4)
O(7)-W(2)-O(6)	90.7(4)	C(3)#5-N(5)-C(3)	97.4(18)
O(11)-W(2)-O(5)	100.1(5)	C(3)#5-N(5)-Cu(2)#9	131.3(9)
O(7)-W(2)-O(5)	156.6(4)	C(3)-N(5)-Cu(2)#9	131.3(9)
O(6)-W(2)-O(5)	87.0(4)	Cu(1)-O(1)-Cu(1)#5	121.3(8)
O(11)-W(2)-O(10)#3	103.1(5)	Cu(1)-O(1)-Cu(2)	119.3(4)
O(7)-W(2)-O(10)#3	85.5(4)	Cu(1)#5-O(1)-Cu(2)	119.3(4)
O(6)-W(2)-O(10)#3	157.0(4)	W(3)-O(2)-Cu(1)	167.3(8)
O(5)-W(2)-O(10)#3	87.6(4)	W(1)-O(3)-W(3)	150.5(5)
O(11)-W(2)-O(8)	170.0(4)	W(2)-O(5)-W(1)	126.3(5)
O(7)-W(2)-O(8)	84.3(4)	W(2)-O(6)-W(3)#1	124.0(5)
O(6)-W(2)-O(8)	73.1(4)	W(2)-O(7)-W(3)#3	151.7(6)
O(5)-W(2)-O(8)	72.8(4)	P(1)-O(8)-W(3)#1	129.5(5)
O(10)#3-W(2)-O(8)	83.9(4)	P(1)-O(8)-W(2)	123.5(5)

O(2)-W(3)-O(3)	101.5(5)	W(3)#1-O(8)-W(2)	88.7(3)
O(2)-W(3)-O(6)#3	101.1(5)	P(1)-O(8)-W(1)	125.6(5)
O(3)-W(3)-O(6)#3	157.4(4)	W(3)#1-O(8)-W(1)	88.8(3)
O(2)-W(3)-O(9)#3	100.1(5)	W(2)-O(8)-W(1)	88.3(3)
O(3)-W(3)-O(9)#3	90.1(4)	W(1)-O(9)-W(3)#1	123.6(5)
O(6)#3-W(3)-O(9)#3	87.4(4)	W(1)-O(10)-W(2)#1	152.0(6)
O(2)-W(3)-O(7)#1	103.7(5)	W(2)-O(11)-Cu(2)#10	156.0(6)
O(3)-W(3)-O(7)#1	85.3(4)	O(13')-O(13)-Cu(1)	82(4)
O(6)#3-W(3)-O(7)#1	87.9(4)	Cu(3)#8-O(14)-Cu(3)	16.3(3)
O(9)#3-W(3)-O(7)#1	156.2(4)	Cu(3)-O(15)-Cu(3)#8	15.8(3)
O(2)-W(3)-O(8)#3	172.6(4)		

Symmetry operation: #1 -y+3/4, x-1/4, -z+1/4; #2 -x+1, -y+1/2, z; #3 y+1/4, -x+3/4, -z+1/4; #4 x, y+1/2, -z; #5 -x+1/2, y, -z; #6 y-1/4, x+1/4, -z+1/4; #7 -y+3/4, x+1/4, z-1/4; #8 -x+1, -y+3/2, z; #9 x, y-1/2, -z; #10 y-1/4, -x+3/4, z+1/4.

Table S2 Selected bond lengths (Å) and bond angles (°) of **2**

O(14)-Cu(1)	2.58(3)	O(6)#2-W(3)-O(4)	156.1(6)
O(13)-Cu(1)	2.60(2)	O(10)-W(3)-O(3)#1	99.9(6)
P(1)-O(11)	1.544(13)	O(9)-W(3)-O(3)#1	158.2(6)
P(1)-O(11)#1	1.544(13)	O(6)#2-W(3)-O(3)#1	87.9(6)
P(1)-O(11)#2	1.544(13)	O(4)-W(3)-O(3)#1	88.4(6)
P(1)-O(11)#3	1.544(13)	O(10)-W(3)-O(11)	171.7(6)
W(1)-O(7)	1.730(14)	O(9)-W(3)-O(11)	84.4(5)
W(1)-O(5)	1.906(15)	O(6)#2-W(3)-O(11)	73.4(5)
W(1)-O(9)	1.920(14)	O(4)-W(3)-O(11)	82.9(5)
W(1)-O(6)	1.922(14)	O(3)#1-W(3)-O(11)	74.1(5)
W(1)-O(8)	1.934(13)	N(3)#4-Cu(3)-N(3)	95(2)
W(1)-O(11)#3	2.463(13)	N(3)#4-Cu(3)-N(4)	169.2(17)
W(2)-O(2)	1.704(14)	N(3)-Cu(3)-N(4)	89.2(17)
W(2)-O(4)	1.894(13)	N(3)#4-Cu(3)-N(4)#4	89.2(17)
W(2)-O(3)	1.926(15)	N(3)-Cu(3)-N(4)#4	169.2(17)
W(2)-O(5)	1.940(14)	N(4)-Cu(3)-N(4)#4	88(3)
W(2)-O(8)#3	1.962(14)	N(3)#4-Cu(3)-N(4')#4	83(3)
W(2)-O(11)#1	2.457(13)	N(3)-Cu(3)-N(4')#4	163(3)
W(3)-O(10)	1.746(15)	N(4)-Cu(3)-N(4')#4	90(3)
W(3)-O(9)	1.931(14)	N(4)#4-Cu(3)-N(4')#4	28(3)
W(3)-O(6)#2	1.959(13)	N(3)#4-Cu(3)-N(4')	163(3)
W(3)-O(4)	1.962(13)	N(3)-Cu(3)-N(4')	83(3)
W(3)-O(3)#1	1.971(14)	N(4')#4-Cu(3)-N(4')	103(6)
W(3)-O(11)	2.433(13)	O(1)-Cu(1)-N(2)	88.9(8)
Cu(3)-N(3)#4	2.02(3)	O(1)-Cu(1)-N(7)	88.5(7)
Cu(3)-N(3)	2.02(3)	N(2)-Cu(1)-N(7)	176.0(9)
Cu(3)-N(4)	2.07(5)	O(1)-Cu(1)-O(10)#5	175.3(5)

Cu(3)-N(4)#4	2.07(5)	N(2)-Cu(1)-O(10)#5	93.4(7)
Cu(3)-N(4')#4	2.10(5)	N(7)-Cu(1)-O(10)#5	89.5(7)
Cu(3)-N(4')	2.10(5)	O(1)-Cu(1)-O(14)	88.9(6)
Cu(1)-O(1)	1.955(10)	N(2)-Cu(1)-O(14)	87.2(10)
Cu(1)-N(2)	1.96(2)	N(7)-Cu(1)-O(14)	89.8(9)
Cu(1)-N(7)	1.960(17)	O(10)#5-Cu(1)-O(14)	95.4(8)
Cu(1)-O(10)#5	1.976(15)	O(1)-Cu(1)-O(13)	95.2(5)
Cu(2)-N(1)#6	1.997(18)	N(2)-Cu(1)-O(13)	94.6(9)
Cu(2)-N(1)	1.997(18)	N(7)-Cu(1)-O(13)	88.6(8)
Cu(2)-O(1)	2.01(2)	O(10)#5-Cu(1)-O(13)	80.5(7)
Cu(2)-N(6)	2.01(2)	O(14)-Cu(1)-O(13)	175.6(8)
Cu(2)-O(2)	2.404(14)	N(1)#6-Cu(2)-N(1)	175.4(10)
Cu(2)-O(2)#6	2.404(14)	N(1)#6-Cu(2)-O(1)	87.7(5)
N(6)-C(3)#7	1.34(3)	N(1)-Cu(2)-O(1)	87.7(5)
N(6)-C(3)#8	1.34(3)	N(1)#6-Cu(2)-N(6)	92.3(5)
N(7)-C(3)	1.30(3)	N(1)-Cu(2)-N(6)	92.3(5)
N(7)-N(7)#6	1.37(3)	O(1)-Cu(2)-N(6)	180
C(1)-N(1)	1.33(3)	N(1)#6-Cu(2)-O(2)	97.4(7)
C(1)-N(3)	1.34(4)	N(1)-Cu(2)-O(2)	82.6(7)
C(2)-N(2)	1.27(3)	O(1)-Cu(2)-O(2)	89.8(4)
C(2)-N(3)	1.35(3)	N(6)-Cu(2)-O(2)	90.2(4)
N(1)-N(2)	1.35(3)	N(1)#6-Cu(2)-O(2)#6	82.6(7)
C(4)-N(4)	1.39(7)	N(1)-Cu(2)-O(2)#6	97.4(7)
C(4)-N(5)	1.45(6)	O(1)-Cu(2)-O(2)#6	89.8(4)
N(4)-N(4)#9	1.41(9)	N(6)-Cu(2)-O(2)#6	90.2(4)
C(4')-N(4')	1.42(7)	O(2)-Cu(2)-O(2)#6	179.6(7)
C(4')-N(5')	1.45(7)	W(1)-O(5)-W(2)	150.3(8)
O(11)-P(1)-O(11)#1	110.1(10)	W(2)-O(3)-W(3)#1	122.8(7)
O(11)-P(1)-O(11)#2	109.2(5)	W(2)-O(4)-W(3)	151.1(8)
O(11)#1-P(1)-O(11)#2	109.2(5)	W(1)-O(8)-W(2)#2	125.0(7)
O(11)-P(1)-O(11)#3	109.2(5)	W(1)-O(9)-W(3)	150.5(8)
O(11)#1-P(1)-O(11)#3	109.2(5)	W(3)-O(10)-Cu(1)#7	168.0(9)
O(11)#2-P(1)-O(11)#3	110.1(10)	W(2)-O(2)-Cu(2)	157.1(8)
O(7)-W(1)-O(5)	102.6(7)	W(1)-O(6)-W(3)#3	124.3(7)
O(7)-W(1)-O(9)	102.1(7)	P(1)-O(11)-W(3)	127.3(7)
O(5)-W(1)-O(9)	87.0(6)	P(1)-O(11)-W(2)#1	124.4(7)
O(7)-W(1)-O(6)	100.0(7)	W(3)-O(11)-W(2)#1	88.8(4)
O(5)-W(1)-O(6)	87.6(6)	P(1)-O(11)-W(1)#2	126.1(7)
O(9)-W(1)-O(6)	157.9(6)	W(3)-O(11)-W(1)#2	89.0(4)
O(7)-W(1)-O(8)	102.1(7)	W(2)#1-O(11)-W(1)#2	89.3(4)
O(5)-W(1)-O(8)	155.3(6)	Cu(1)#6-O(1)-Cu(1)	120.7(10)
O(9)-W(1)-O(8)	87.8(5)	Cu(1)#6-O(1)-Cu(2)	119.7(5)
O(6)-W(1)-O(8)	88.2(6)	Cu(1)-O(1)-Cu(2)	119.7(5)
O(7)-W(1)-O(11)#3	171.5(6)	C(3)#7-N(6)-C(3)#8	102(3)

O(5)-W(1)-O(11)#3	82.6(6)	C(3)#7-N(6)-Cu(2)	129.1(13)
O(9)-W(1)-O(11)#3	84.8(5)	C(3)#8-N(6)-Cu(2)	129.1(13)
O(6)-W(1)-O(11)#3	73.2(5)	C(3)-N(7)-N(7)#6	105.8(13)
O(8)-W(1)-O(11)#3	72.9(5)	C(3)-N(7)-Cu(1)	132.9(16)
O(2)-W(2)-O(4)	102.6(6)	N(7)#6-N(7)-Cu(1)	121.2(5)
O(2)-W(2)-O(3)	98.9(6)	N(1)-C(1)-N(3)	112(2)
O(4)-W(2)-O(3)	90.0(6)	N(2)-C(2)-N(3)	114(2)
O(2)-W(2)-O(5)	102.7(7)	N(7)-C(3)-N(6)#10	113(2)
O(4)-W(2)-O(5)	86.8(6)	C(1)-N(1)-N(2)	105.8(19)
O(3)-W(2)-O(5)	158.3(6)	C(1)-N(1)-Cu(2)	132.8(17)
O(2)-W(2)-O(8)#3	100.8(6)	N(2)-N(1)-Cu(2)	120.2(13)
O(4)-W(2)-O(8)#3	156.7(6)	C(2)-N(2)-N(1)	107(2)
O(3)-W(2)-O(8)#3	87.5(6)	C(2)-N(2)-Cu(1)	130.6(18)
O(5)-W(2)-O(8)#3	87.0(6)	N(1)-N(2)-Cu(1)	122.6(15)
O(2)-W(2)-O(11)#1	170.4(6)	C(1)-N(3)-C(2)	101(2)
O(4)-W(2)-O(11)#1	84.4(5)	C(1)-N(3)-Cu(3)	123.4(19)
O(3)-W(2)-O(11)#1	74.2(5)	C(2)-N(3)-Cu(3)	133(2)
O(5)-W(2)-O(11)#1	84.1(6)	N(4)-C(4)-N(5)	107(5)
O(8)#3-W(2)-O(11)#1	72.6(5)	C(4)-N(4)-N(4)#9	108(4)
O(10)-W(3)-O(9)	101.8(7)	C(4)-N(4)-Cu(3)	123(4)
O(10)-W(3)-O(6)#2	101.1(6)	N(4)#9-N(4)-Cu(3)	126(3)
O(9)-W(3)-O(6)#2	89.4(6)	C(4)#9-N(5)-C(4)	106(7)
O(10)-W(3)-O(4)	102.8(6)	N(4')-C(4')-N(5')	106(6)
O(9)-W(3)-O(4)	85.4(6)	C(4')-N(4')-Cu(3)	115(5)

Symmetry opetation:#1 -x+1, -y+1/2, z; #2 y+1/4, -x+3/4, -z+1/4; #3 -y+3/4, x-1/4, -z+1/4; #4 -x, -y+1/2, z; #5 -x+1/2, y-1/2, z; #6 -x+1/2, y, -z; #7 -x+1/2, y+1/2, z; #8 x, y+1/2, -z; #9 -y+1/4, -x+1/4, -z+1/4; #10 x, y-1/2, -z.

Table S3 BVS Calculations of **1**

Atom 1	Atom 2	R_0 value	B value	Length (Å)	Valence
Cu1	N2	1.574	0.370	1.976	0.338
Cu1	N4	1.574	0.370	1.996	0.320
Cu1	O1	1.679	0.370	1.968	0.456
Cu1	O2	1.679	0.370	1.956	0.473
Cu1	O12	1.679	0.370	2.585	0.086
Cu1	O13	1.679	0.370	2.598	0.083
Cu2	N1	1.574	0.370	2.021	0.299
Cu2	N5	1.574	0.370	1.982	0.332
Cu2	O1	1.679	0.370	2.032	0.385
Cu2	O11	1.679	0.370	2.401	0.142
Cu3	N3	1.574	0.370	1.998*	0.318
Cu3	O14	1.600	0.370	2.20*	0.198

Cu3	O15	1.600	0.370	2.19*	0.203

*Average distance.

Table S4 Valence of Selected Atoms of **1**

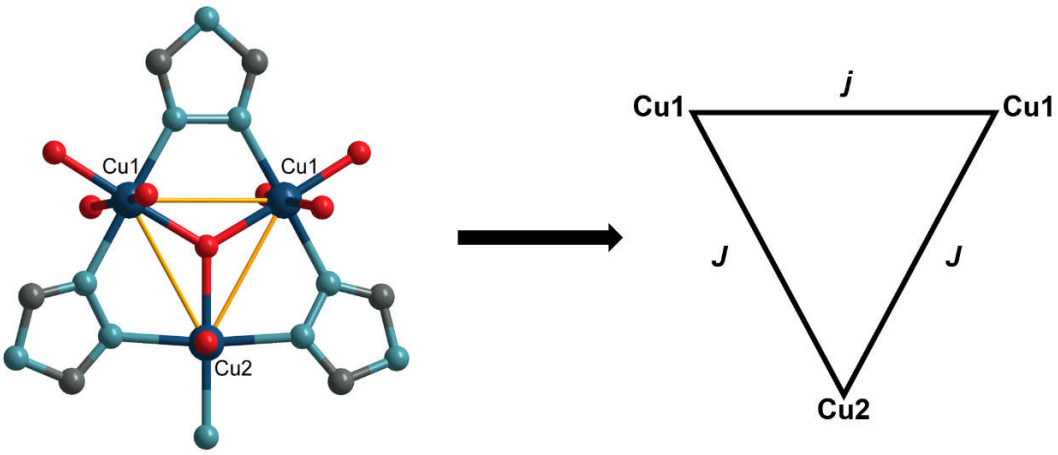
Atom	Valence
Cu1	1.756
Cu2	1.599
Cu3	1.037
O1	1.297
O12	0.086
O13	0.083
O14	0.198
O15	0.203

Table S5 BVS Calculations of **2**

Atom 1	Atom 2	R_0 value	B value	Length (Å)	Valence
Cu1	N2	1.574	0.370	1.96	0.353
Cu1	N7	1.574	0.370	1.960	0.353
Cu1	O1	1.679	0.370	1.955	0.474
Cu1	O10	1.679	0.370	1.976	0.448
Cu1	O13	1.679	0.370	2.58	0.088
Cu1	O14	1.679	0.370	2.60	0.083
Cu2	N1	1.574	0.370	1.997	0.319
Cu2	N6	1.574	0.370	2.01	0.308
Cu2	O1	1.679	0.370	2.01	0.409
Cu2	O2	1.679	0.370	2.404	0.141
Cu3	N3	1.574	0.370	2.02	0.300
Cu3	N4	1.574	0.370	2.07	0.262

Table S6 Valence of Selected Atoms of **2**

Atom	Valence
Cu1	1.799
Cu2	1.637
Cu3	1.124
O1	1.357
O13	0.088
O14	0.083



Scheme S1 Exchange effect in tricopper units

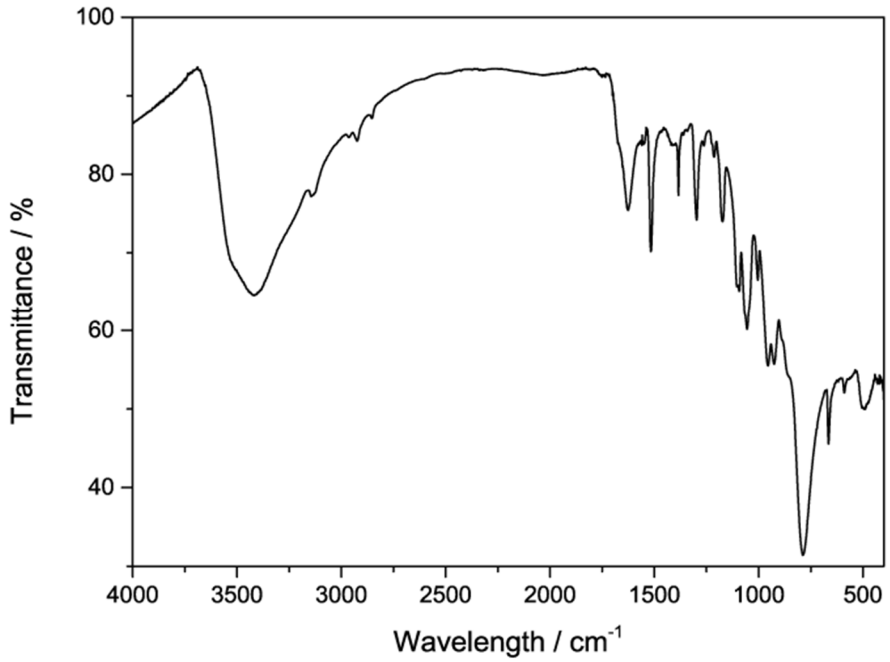


Figure S1 FT-IR spectrum of **1**

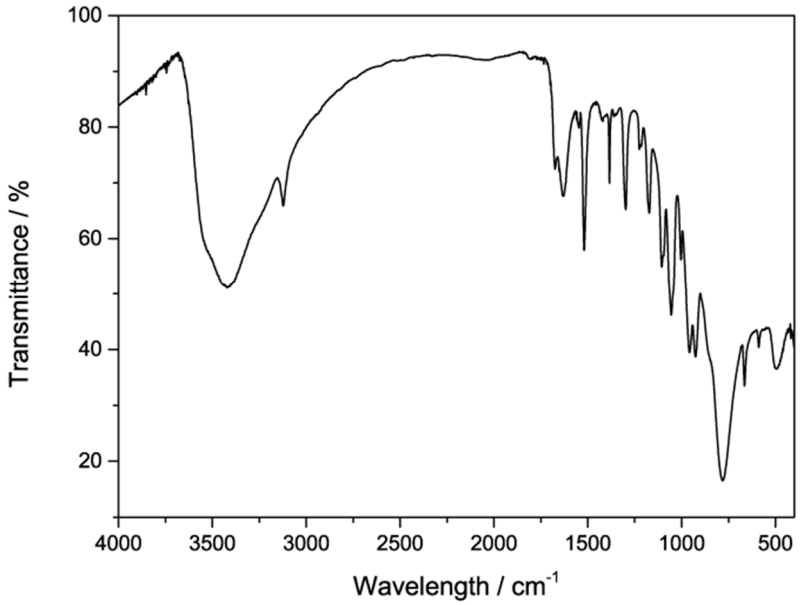


Figure S2 FT-IR spectrum of **2**

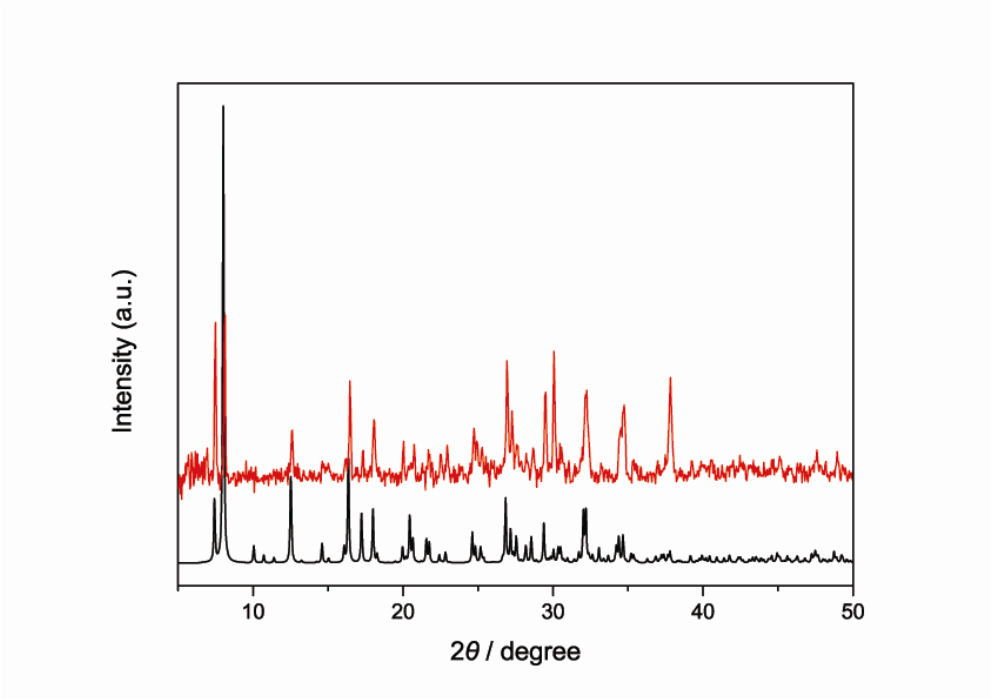


Figure S3 Experimental powder XRD pattern of **1** (red) compared to simulated pattern from the crystal structure (black).

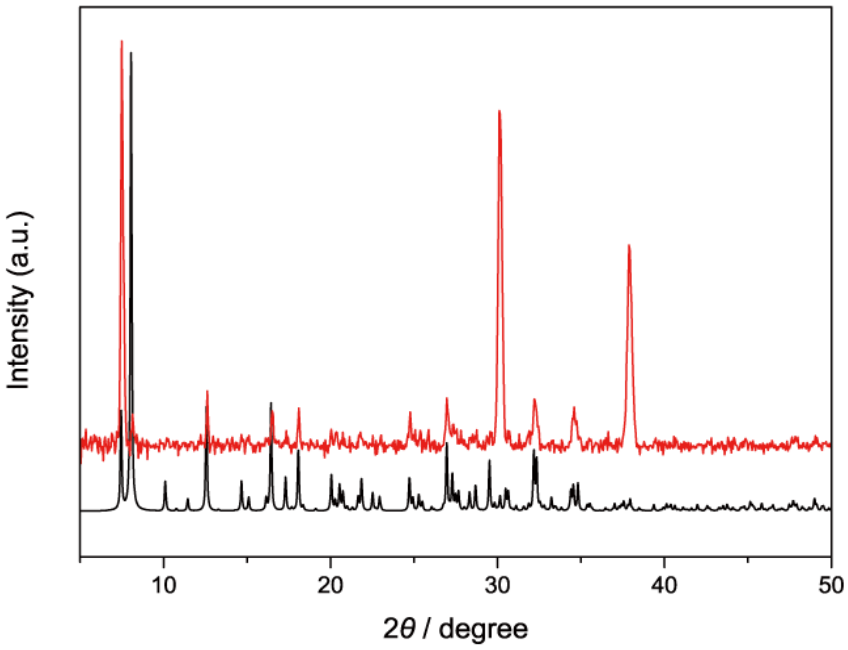


Figure S4 Experimental powder XRD pattern of **2** (red) compared to simulated pattern from the crystal structure (black).

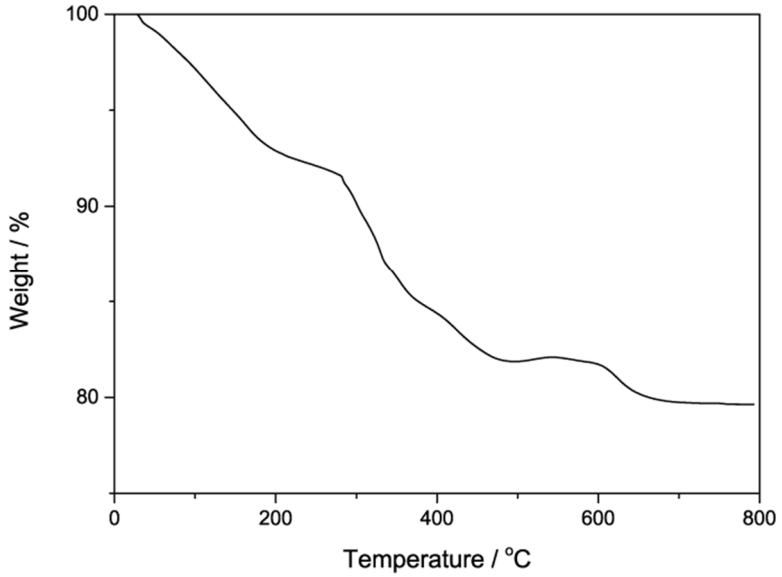


Figure S5 The TG curve of **1**

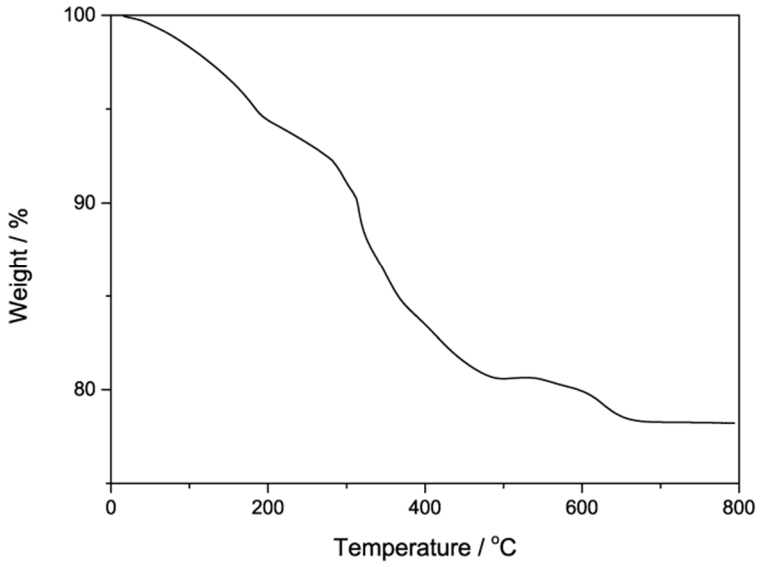


Figure S6 The TG curve of **2**

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