Electronic Supplementary Information

Three New POM-based Coordination Polymers with 1, 3, 5-tris (1-imidazolyl)benzene Ligand: Syntheses, Structures and Proton Conductivity

Lin-Lin Chen,‡ Ya-Jie Shi,‡ Wen-Wen Wu, Jia-Xin Wang, Ya-Min Li,* Yan Bai and Dong-Bin Dang*

Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, China

Additional Figures

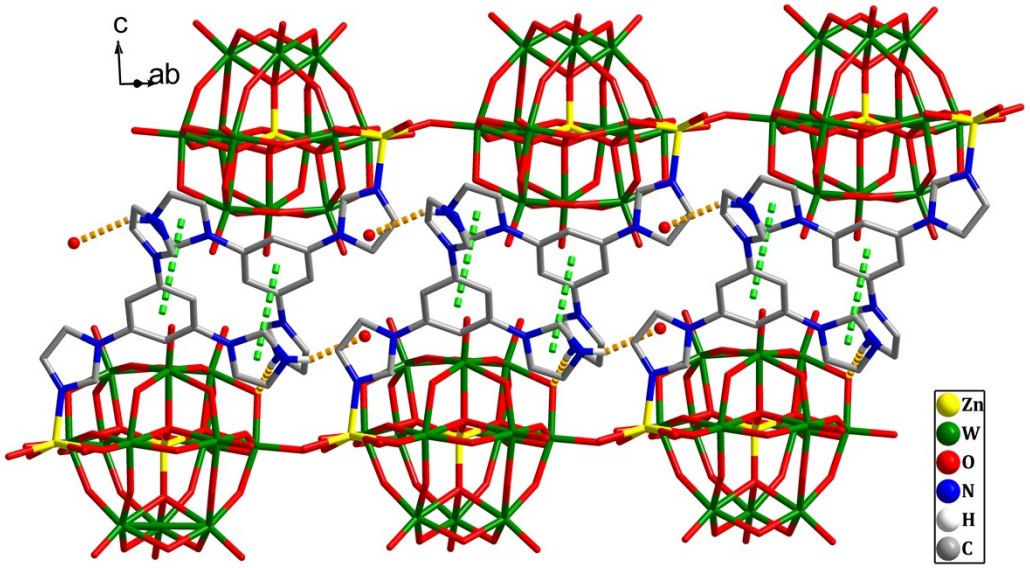


Fig. S1 π-π interactions and hydrogen-bonding interactions in two neighboring 2D layers B in compound **2**.

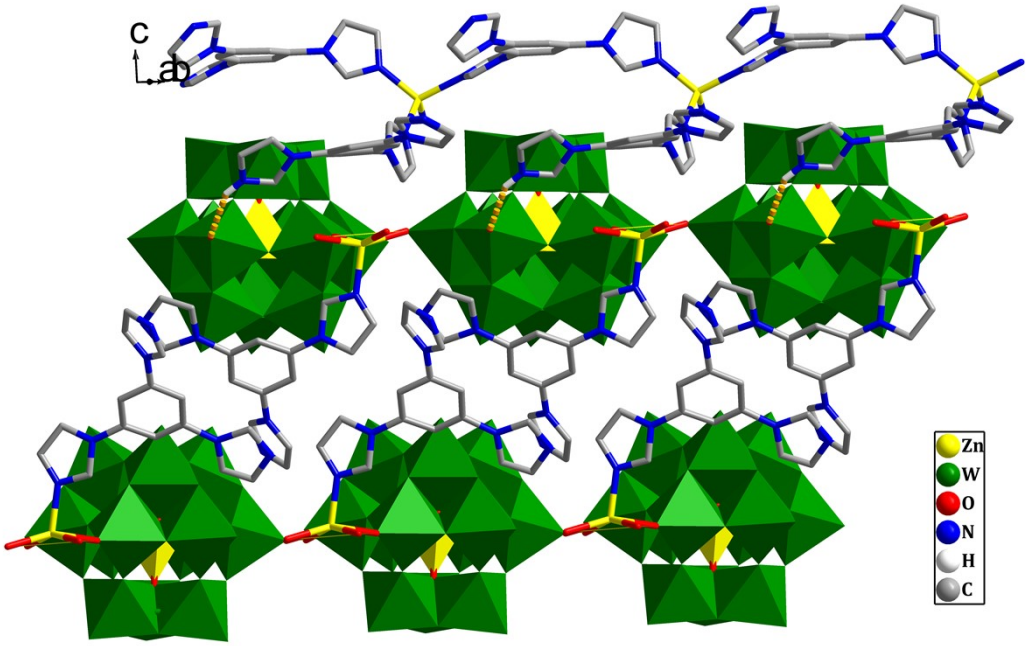


Fig. S2 Hydrogen-bonding interactions between 2D layer A and bilayer B in compound **2**

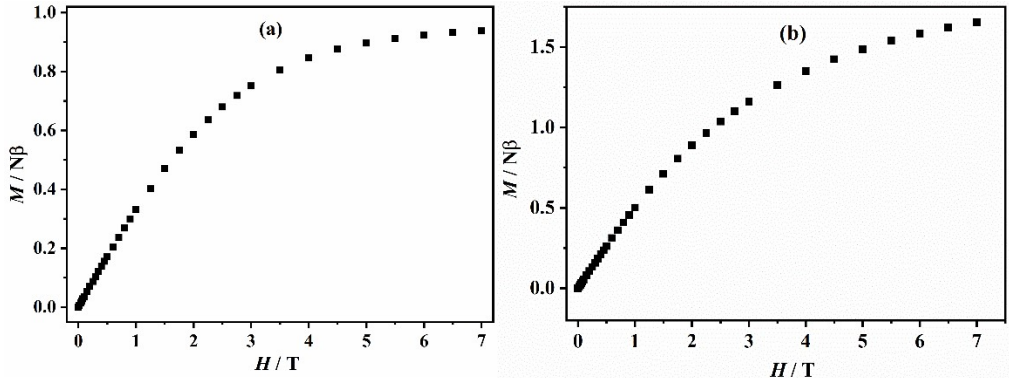


Fig. S3 Isothermal magnetization of **1** (a) and **3** (b) at 2 K.

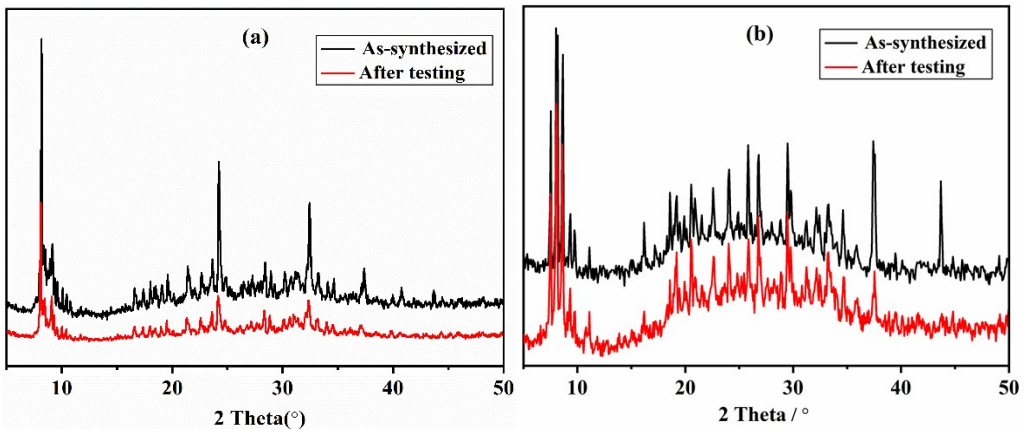


Fig. S4 The powder X-ray diffraction patterns of **2** (a) and **3** (b) before and after testing.

PXRD

X-ray powder diffraction test analyses of compounds **1-3** were conducted in the range of 2θ = 5-50º. As shown in Fig. S**5**, the peak position of the experimental PXRD is basically consistent with the theoretical peak position of the measured data of single crystal structure. PXRD data of compounds **1-3** suggest that the samples are of high purity and retain their crystallinity. The difference of peak strength mainly contributes to the preparation of samples before the test and the different orientations during the test.

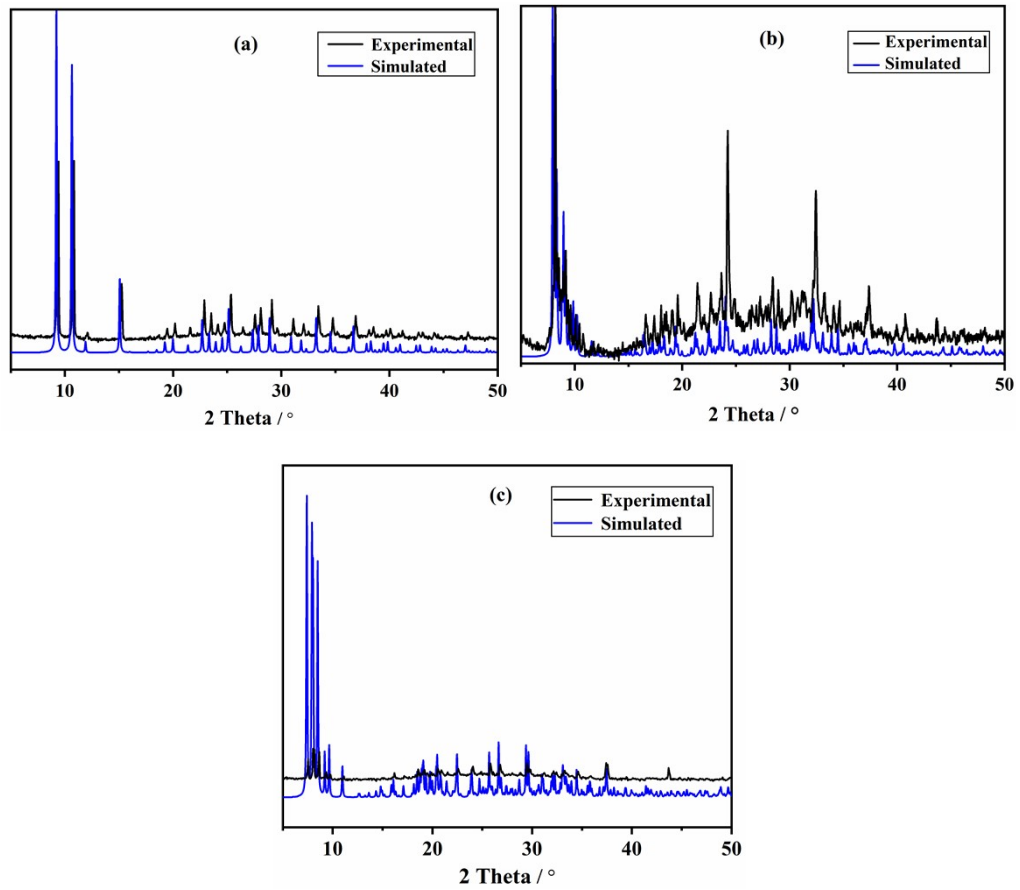


Fig. S5 PXRD patterns of compounds **1** (a), **2** (b) and **3** (c).

TG Analysis

The thermogravimetric analyses have been performed on the thermal stability of compounds **1-3**. They were tested under N_2 atmosphere at temperature range of 25 - 1000 ºC with a rate of 10 ºC/minutes. As shown in Fig. S**6**, since there are no water molecules in compound **1**, the weight loss curve does not decrease as the temperature rise at the beginning, whereas both compounds **2** and **3** show two-step weight loss. As the temperature gradually increases, the weight loss curves of compounds **2** and **3** gradually decrease, which is mainly attributed to the loss of water molecules in compounds. With the temperature rising continually, the weight of the compounds **1-3** drop sharply in the temperature range above 450ºC, 431ºC, and 455ºC, respectively, attributed to the loss of all organic ligands and the collapse of the skeleton. Their frameworks also preserve the structural integrity up to 431 ºC. The different thermal stability between compounds **1-3** is mainly due to the difference of complex structure.

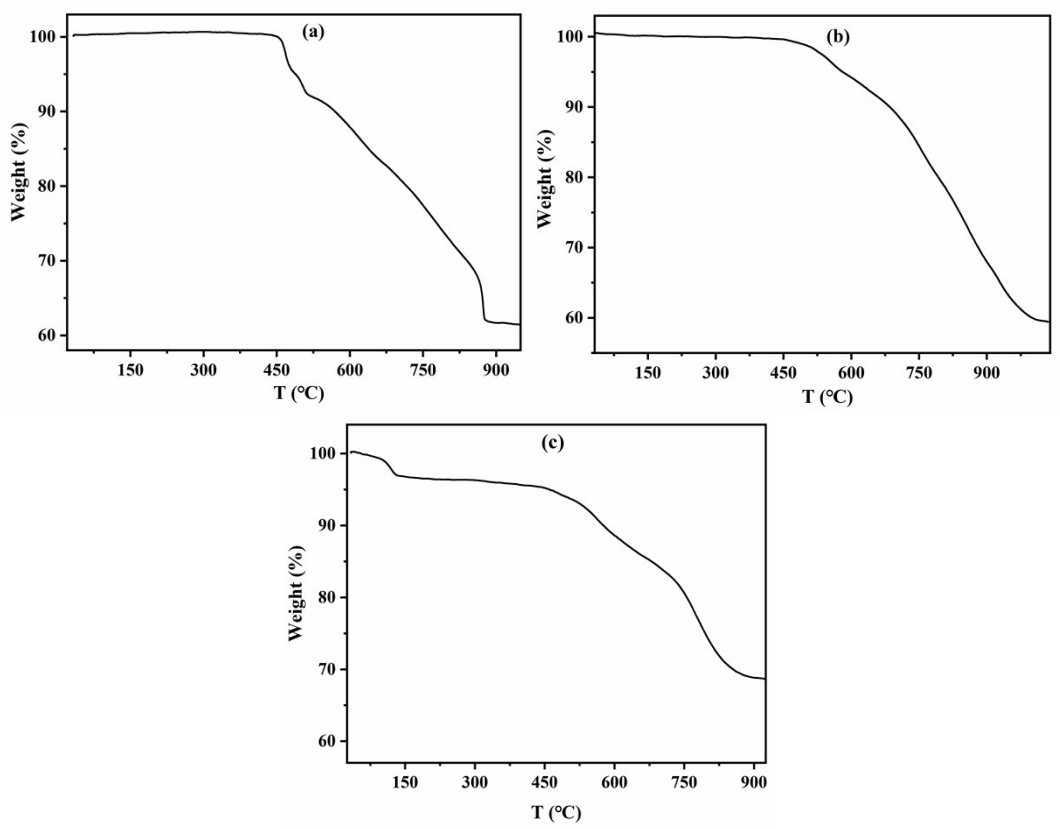
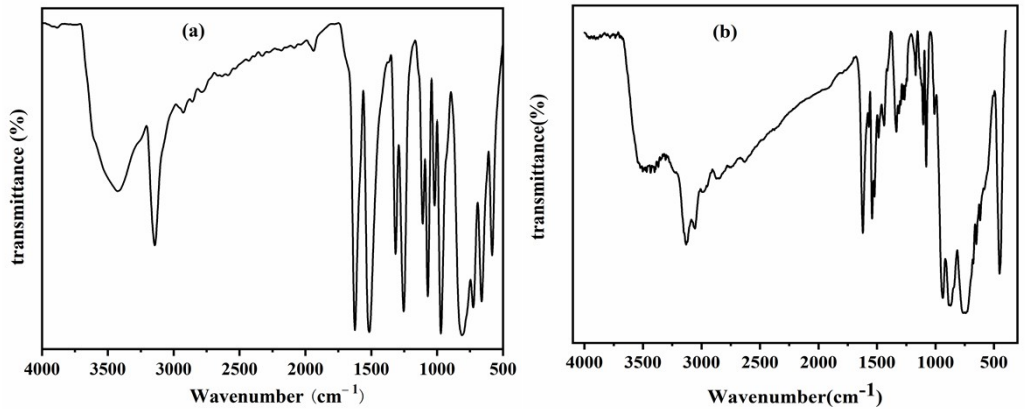


Fig. S6 TGA curves of compounds **1** (a), **2** (b) and **3** (c).

IR spectra

The FT-IR spectra of compounds **1-3** are displayed in Fig. S**7**. The absorption peak in the range of 700-1100 cm^{-1} is mainly derived from the stretching vibration of W-$O_{b/c/d}$ bond in the polyacid anion (b/c: bridge oxygen, d: terminal oxygen). The characteristic bands observed at 1069, 974, 808, 659 cm^{-1} for **1**, 1009, 940, 880, 747 cm^{-1} for **2**, 1072, 946, 887, 768 cm^{-1} for **3** are attributed to ν(W–O_t), ν(W–O_b–W), ν(W–O_c–W), respectively. In addition, bands observed at 1626, 1521, 1320, 1245 cm^{-1} for **1**, 1629, 1540, 1331, 1104 cm^{-1} for **2,** 1624, 1519, 1323, 1254 cm^{-1} for **3** stem from the C=C/C=N stretching vibrations in the ligands. All above proved the existence of polyacid anions and ligands in compounds **1-3**.



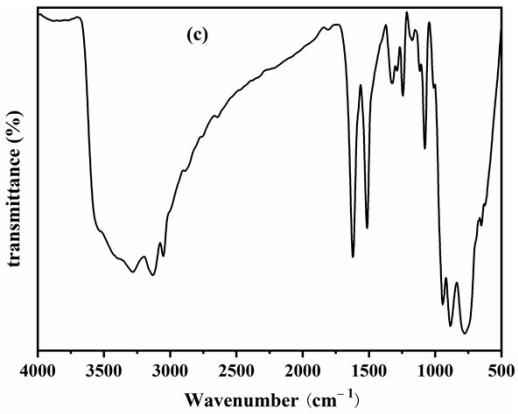


Fig. S7 IR spectra of compounds **1** (a), **2** (b) and **3** (c).

Proton conductivity measurement

Electrochemical impedance spectroscopy was measured on a impedance analyzer Solartron 1260 and 1296 in a frequency range of 1 Hz to 10 MHz at amplitude of 0.01 V. Ac impedance maps were analyzed by Power-Suite, with the resistance value determined from equivalent circuit fits of the first semi-circle using ZView Software. Proton conductivity was calculated using the following equation: $\sigma = L/(RS)$. σ for electrical conductivity ($S \cdot cm^{-1}$); L is the slice thickness (cm); S is piece surface area namely Πr^2 (cm^2) (where r is the radius of the slice. (cm)); R was extracted directly from the impedance plots, which is the bulk resistance of the sample (**Ω**). Activation energy (E_a) was calculated with the Arrhenius equation $\sigma T = \sigma_0 \exp(- Ea/K_B T)$, where σ is the proton conductivity, σ_0 is the preexponential factor, K_B is the Boltzmann constant, and T is the temperature.

Table S1 The selected bond lengths (Å) and angles (°) of compounds **1**-**3**.

Compound 1			
Cu1–N1	2.13(3)	O1–W1^{i}	2.291(7)
Cu1–N1^{iv}	2.13(3)	O1–W1^{ix}	2.291(7)
Cu1–N1^{v}	2.13(3)	O1–W1^{iii}	2.291(7)
Cu1–N1^{vi}	2.13(3)	O1–W1	2.291(7)
Cu1–N1^{vii}	2.13(3)	O1–W1^{ii}	2.291(7)
Cu1–N1^{viii}	2.13(3)	O1–W1^{x}	2.291(7)
O3–W1	1.76(2)	O4–W1	1.74(2)
O2–W1^{i}	2.05(2)	O4–W1^{x}	1.82(2)
O2–W1	2.09(2)	W1^{x}—O1—W1	83.5 (2)
N1^{vii}—Cu1—N1^{iv}	88.9 (11)	W1—O4—W1x	118.2 (12)
N1^{vii}—Cu1—N1	88.9 (11)	O2^{ii}—W1—O2	78.2 (12)
N1^{viii}—Cu1—N1^{v}	88.9 (11)	O2—W1—O1	75.0 (7)
N1^{v}—Cu1—N1	91.1 (11)	O2^{ii}—W1—O1	75.8 (6)
N1^{viii}—Cu1—N1^{vi}	88.9 (11)	O2—W1—W1^{x}	122.8 (6)

N1^{viii}—Cu1—N1	91.1 (11)	O2^{ii}—W1—W1^{x}	81.1 (6)
N1^{vi}—Cu1—N1^{v}	88.9 (11)	O2—W1—W1^{iii}	80.5 (7)
N1^{iv}—Cu1—N1^{v}	180	O2^{ii}—W1—W1^{iii}	123.5 (6)
N1^{vii}—Cu1—N1^{vi}	91.1 (11)	O1—W1—W1^{x}	48.25 (10)
N1^{viii}—Cu1—N1^{vii}	180.0 (9)	O1—W1—W1^{iii}	48.25 (10)
N1^{vi}—Cu1—N1	180	O4—W1—O2^{ii}	90.8 (11)
N1^{iv}—Cu1—N1	88.9 (11)	O4^{iii}—W1—O2^{ii}	152.0 (10)
N1^{viii}—Cu1—N1^{iv}	91.1 (11)	O4—W1—O2	154.4 (10)
N1^{vi}—Cu1—N1^{iv}	91.1 (11)	O4^{iii}—W1—O2	85.1 (11)
N1^{vii}—Cu1—N1^{v}	91.1 (11)	O4—W1—O1	79.9 (8)
W1^{i}—O2—W1	111.4 (11)	O4^{iii}—W1—O1	78.2 (7)
O4—W1—O4^{iii}	94.9 (4)	O4—W1—O3	110.9 (11)
O3—W1—O2	93.6 (10)	O4—W1—W1^{x}	31.7 (8)
O3—W1—O1	167.5 (8)	O3—W1—O2^{ii}	97.1 (10)
O3—W1—O4^{iii}	106.4 (11)		
Compound 2			
Zn1—N1^{i}	1.987 (5)	W9—O26	1.918 (4)
Zn1—N1^{ii}	1.987 (5)	W9—O28	1.970 (5)
Zn1—N4^{iii}	1.993 (5)	W10—O4	2.174 (4)
Zn1—N4	1.993 (5)	W10—O6	1.991 (4)
Zn2—N8	1.997 (6)	W10—O28	1.935 (5)
Zn2—O2W	2.124 (7)	W10—O29	1.955 (5)
Zn2—O7^{iv}	1.979 (4)	W10—O34	1.868 (5)
Zn2—O11^{i}	2.212 (5)	W10—O35	1.719 (5)
Zn2—O20	2.052 (5)	W11—O2	2.208 (4)
Zn3—O2	1.891 (4)	W11—O8	1.967 (5)
Zn3—O3	1.876 (4)	W11—O19	1.924 (5)
Zn3—O4	1.884 (5)	W11—O21	1.925 (4)
Zn3—O17	1.875 (4)	W11—O29	1.893 (5)
W9—O20	1.756 (5)	W11—O36	1.714 (5)
W1—O5	1.878 (4)	W12—O3	2.188 (4)
W1—O14	1.908 (4)	W12—O19	1.890 (5)
W1—O15	1.710 (4)	W12—O31	1.899 (5)
W1—O17	2.183 (4)	W12—O34	1.983 (5)
W1—O25	2.012 (4)	W12—O38	1.980 (5)
W1—O30	1.965 (4)	W12—O40	1.709 (5)
W2—W3	3.2207 (4)	W5—O1	1.933 (4)
W2—O10	1.970 (4)	W5—O4	2.173 (4)
W2—O13	1.994 (4)	W5—O6	1.891 (4)
W2—O17	2.145 (4)	W5—O12	1.708 (4)
W2—O27	1.717 (5)	W5—O26	1.950 (4)

W2—O30	1.908 (4)	W5—O33	1.967 (4)
W2—O32	1.879 (5)	W6—O1	1.899 (4)
W3—O5	2.009 (4)	W6—O2	2.084 (4)
W3—O13	1.872 (4)	W6—O7	1.753 (4)
W3—O16	2.009 (4)	W6—O16	1.841 (4)
W3—O17	2.151 (4)	W6—O21	2.012 (4)
W3—O33	1.876 (4)	W6—O24	1.970 (4)
W3—O39	1.713 (4)	W7—W8	3.2389 (5)
W4—O2	2.176 (4)	W7—O3	2.169 (4)
W4—O8	1.903 (4)	W7—O18	1.921 (5)
W4—O9	1.902 (5)	W7—O23	1.946 (5)
W4—O14	1.924 (4)	W7—O32	1.929 (4)
W4—O22	1.722 (5)	W7—O37	1.728 (5)
W4—O24	1.985 (4)	W7—O38	1.902 (5)
W8—O25	1.847 (4)	W8—O3	2.146 (5)
W8—O31	1.988 (4)	W8—O9	1.953 (5)
W9—O4	2.139 (4)	W8—O11	1.749 (5)
W9—O10	1.869 (4)	W8—O23	1.919 (5)
W9—O18	1.924 (5)		
N1^{i}—Zn1—N1^{ii}	102.1 (3)	O10—W9—O26	92.60 (19)
N1^{ii}—Zn1—N4^{iii}	113.1 (2)	O10—W9—O28	161.33 (19)
N1^{i}—Zn1—N4	113.1 (2)	O18—W9—O4	86.45 (18)
N1^{i}—Zn1—N4^{iii}	109.6 (2)	O18—W9—O28	87.1 (2)
N1^{ii}—Zn1—N4	109.6 (2)	O20—W9—O4	169.5 (2)
N4^{iii}—Zn1—N4	109.4 (3)	O20—W9—O10	100.3 (2)
N8—Zn2—O2W	111.0 (3)	O20—W9—O18	100.1 (2)
N8—Zn2—O11^{i}	92.5 (2)	O20—W9—O26	98.4 (2)
N8—Zn2—O20	92.7 (2)	O20—W9—O28	98.0 (2)
O2W—Zn2—O11^{i}	156.3 (2)	O26—W9—O4	74.96 (18)
O7^{iv}—Zn2—N8	108.4 (2)	O26—W9—O18	161.4 (2)
O7^{iv}—Zn2—O2W	83.7 (2)	O26—W9—O28	88.25 (19)
O7^{iv}—Zn2—O11^{i}	91.40 (19)	O28—W9—O4	73.89 (18)
O7^{iv}—Zn2—O20	158.4 (2)	O6—W10—O4	73.13 (17)
O20—Zn2—O2W	84.6 (2)	O28—W10—O4	73.76 (17)
O20—Zn2—O11^{i}	92.10 (19)	O28—W10—O6	88.93 (19)
O3—Zn3—O2	109.92 (19)	O28—W10—O29	159.84 (18)
O3—Zn3—O4	110.3 (2)	O29—W10—O4	86.10 (17)
O4—Zn3—O2	110.29 (19)	O29—W10—O6	85.83 (18)
O17—Zn3—O2	108.12 (18)	O34—W10—O4	89.18 (18)
O17—Zn3—O3	109.64 (19)	O34—W10—O6	160.51 (19)
O17—Zn3—O4	108.49 (19)	O34—W10—O28	94.0 (2)
O5—W1—W2	83.97 (13)	O34—W10—O29	84.8 (2)

O5—W1—O14	93.63 (18)	O35—W10—O4	165.2 (2)
O5—W1—O17	75.59 (17)	O35—W10—O6	94.9 (2)
O5—W1—O25	160.81 (18)	O35—W10—O28	97.9 (2)
O5—W1—O30	91.46 (18)	O35—W10—O29	102.0 (2)
O14—W1—W2	128.33 (13)	O35—W10—O34	103.7 (2)
O14—W1—O17	88.18 (17)	O8—W11—O2	73.17 (17)
O14—W1—O25	83.02 (17)	O19—W11—O2	88.65 (17)
O14—W1—O30	159.47 (18)	O19—W11—O8	86.88 (19)
O15—W1—W2	132.20 (15)	O19—W11—O21	161.34 (18)
O15—W1—O5	101.3 (2)	O21—W11—O2	72.81 (17)
O15—W1—O14	98.99 (19)	O21—W11—O8	89.72 (18)
O15—W1—O17	172.41 (19)	O29—W11—O2	87.33 (17)
O15—W1—O25	97.9 (2)	O29—W11—O8	159.32 (18)
O15—W1—O30	99.5 (2)	O29—W11—O19	85.79 (19)
O17—W1—W2	41.15 (11)	O29—W11—O21	91.07 (18)
O25—W1—W2	83.40 (13)	O36—W11—O2	167.3 (2)
O25—W1—O17	85.40 (17)	O36—W11—O8	99.7 (2)
O30—W1—W2	32.74 (13)	O36—W11—O19	101.6 (2)
O30—W1—O17	73.86 (17)	O36—W11—O21	97.1 (2)
O30—W1—O25	85.66 (18)	O36—W11—O29	100.7 (2)
W3—W2—W1	60.433 (9)	O19—W12—O3	88.79 (18)
O10—W2—W1	127.26 (13)	O19—W12—O31	93.7 (2)
O10—W2—W3	82.77 (13)	O19—W12—O34	84.9 (2)
O10—W2—O13	85.50 (18)	O19—W12—O38	158.92 (19)
O10—W2—O17	85.27 (17)	O31—W12—O3	74.40 (18)
O13—W2—W1	81.93 (12)	O31—W12—O34	160.14 (19)
O13—W2—W3	32.42 (12)	O31—W12—O38	91.0 (2)
O13—W2—O17	73.87 (17)	O34—W12—O3	85.75 (18)
O17—W2—W1	42.04 (11)	O38—W12—O3	72.71 (17)
O17—W2—W3	41.51 (11)	O38—W12—O34	83.77 (19)
O27—W2—W1	132.35 (15)	O40—W12—O3	167.7 (2)
O27—W2—W3	127.46 (16)	O40—W12—O19	102.6 (2)
O27—W2—O10	99.6 (2)	O40—W12—O31	99.8 (2)
O27—W2—O13	95.1 (2)	O40—W12—O34	99.8 (2)
O27—W2—O17	167.66 (19)	O40—W12—O38	96.8 (2)
O27—W2—O30	99.1 (2)	O13—W3—O16	161.35 (18)
O27—W2—O32	102.5 (2)	O13—W3—O17	76.14 (17)
O30—W2—W1	33.85 (13)	O13—W3—O33	95.60 (18)
O30—W2—W3	83.69 (13)	O16—W3—W2	126.56 (12)
O30—W2—O10	161.11 (18)	O16—W3—O17	85.21 (16)
O30—W2—O13	90.10 (18)	O17—W3—W2	41.38 (11)
O30—W2—O17	75.86 (17)	O33—W3—W2	91.92 (13)
O32—W2—W1	90.73 (14)	O33—W3—O5	160.18 (18)

O32—W2—W3	129.85 (13)	O33—W3—O16	84.42 (18)
O32—W2—O10	85.33 (19)	O33—W3—O17	89.44 (18)
O32—W2—O13	161.28 (18)	O39—W3—W2	134.54 (14)
O32—W2—O17	89.13 (18)	O39—W3—O5	94.60 (19)
O32—W2—O30	93.33 (19)	O5—W3—O17	73.80 (16)
O5—W3—W2	82.54 (12)	O13—W3—W2	34.82 (13)
O5—W3—O16	83.70 (17)	O13—W3—O5	90.66 (18)
O39—W3—O13	100.32 (19)	W6—O1—W5	150.7 (3)
O39—W3—O16	97.85 (19)	Zn3—O2—W4	119.3 (2)
O39—W3—O17	167.68 (19)	Zn3—O2—W6	119.3 (2)
O39—W3—O33	102.7 (2)	Zn3—O2—W11	117.2 (2)
O8—W4—O2	75.11 (17)	W4—O2—W11	96.32 (17)
O8—W4—O14	159.78 (18)	W6—O2—W4	100.57 (17)
O8—W4—O24	89.66 (18)	W6—O2—W11	99.89 (17)
O9—W4—O2	90.73 (18)	Zn3—O3—W7	118.7 (2)
O9—W4—O8	91.68 (19)	Zn3—O3—W8	120.9 (2)
O9—W4—O14	85.60 (18)	Zn3—O3—W12	119.7 (2)
O9—W4—O24	162.16 (19)	W7—O3—W12	97.55 (17)
O14—W4—O2	84.88 (17)	W8—O3—W7	97.30 (18)
O14—W4—O24	87.01 (17)	W8—O3—W12	97.65 (18)
O22—W4—O2	167.29 (19)	Zn3—O4—W5	120.2 (2)
O22—W4—O8	100.1 (2)	Zn3—O4—W9	119.9 (2)
O22—W4—O9	101.3 (2)	Zn3—O4—W10	118.5 (2)
O22—W4—O14	100.1 (2)	W5—O4—W10	97.36 (17)
O22—W4—O24	96.0 (2)	W9—O4—W5	97.49 (18)
O24—W4—O2	72.44 (16)	W9—O4—W10	98.53 (17)
O1—W5—O4	88.49 (18)	W1—O5—W3	113.4 (2)
O1—W5—O26	160.51 (19)	W5—O6—W10	114.5 (2)
O1—W5—O33	83.29 (18)	W6—O7—Zn2^{vi}	147.8 (3)
O6—W5—O1	91.30 (19)	W4—O8—W11	115.2 (2)
O6—W5—O4	75.03 (17)	W4—O9—W8	150.2 (3)
O6—W5—O26	91.24 (19)	W9—O10—W2	151.4 (3)
O6—W5—O33	160.63 (19)	W8—O11—Zn2^{v}	164.1 (3)
O12—W5—O1	101.8 (2)	W3—O13—W2	112.8 (2)
O12—W5—O4	167.82 (19)	W1—O14—W4	154.7 (2)
O12—W5—O6	98.1 (2)	W6—O16—W3	148.8 (2)
O12—W5—O26	96.9 (2)	Zn3—O17—W1	119.6 (2)
O12—W5—O33	101.3 (2)	Zn3—O17—W2	119.8 (2)
O26—W5—O4	73.54 (17)	Zn3—O17—W3	120.9 (2)
O26—W5—O33	87.97 (18)	W2—O17—W1	96.81 (16)
O33—W5—O4	86.21 (17)	W2—O17—W3	97.12 (17)
O1—W6—O2	89.56 (18)	W3—O17—W1	97.16 (16)
O1—W6—O21	87.08 (18)	W7—O18—W9	152.2 (3)

O1—W6—O24	164.31 (18)	W12—O19—W11	152.5 (3)
O7—W6—O1	101.1 (2)	W9—O20—Zn2	151.7 (3)
O7—W6—O2	163.05 (19)	W11—O21—W6	113.1 (2)
O7—W6—O16	102.7 (2)	W8—O23—W7	113.9 (2)
O7—W6—O21	93.30 (19)	W6—O24—W4	112.0 (2)
O7—W6—O24	93.85 (19)	W8—O25—W1	153.4 (2)
O16—W6—O1	89.04 (18)	W9—O26—W5	113.9 (2)
O16—W6—O2	90.48 (17)	W10—O28—W9	113.6 (2)
O16—W6—O21	163.95 (18)	W11—O29—W10	152.8 (2)
O16—W6—O24	92.40 (18)	W2—O30—W1	113.4 (2)
O21—W6—O2	73.93 (17)	W12—O31—W8	114.1 (2)
O24—W6—O2	74.80 (17)	W2—O32—W7	154.0 (3)
O24—W6—O21	87.25 (18)	W3—O33—W5	154.9 (3)
O3—W7—W8	41.08 (12)	W10—O34—W12	152.9 (3)
O18—W7—W8	129.44 (14)	W7—O38—W12	115.1 (2)
O18—W7—O3	89.07 (18)	O11—W8—O3	168.14 (19)
O18—W7—O23	161.87 (19)	O11—W8—O9	98.8 (2)
O18—W7—O32	84.34 (19)	O11—W8—O23	98.9 (2)
O23—W7—W8	32.82 (13)	O11—W8—O25	102.2 (2)
O23—W7—O3	73.74 (18)	O11—W8—O31	96.3 (2)
O32—W7—W8	84.51 (13)	O23—W8—W7	33.33 (14)
O32—W7—O3	86.32 (17)	O23—W8—O3	74.79 (18)
O32—W7—O23	88.76 (19)	O23—W8—O9	161.9 (2)
O37—W7—W8	131.92 (17)	O23—W8—O31	87.88 (19)
O37—W7—O3	169.8 (2)	O25—W8—W7	89.30 (14)
O37—W7—O18	98.6 (2)	O25—W8—O3	88.43 (18)
O37—W7—O23	99.2 (2)	O25—W8—O9	85.95 (18)
O37—W7—O32	101.0 (2)	O25—W8—O23	94.08 (19)
O37—W7—O38	98.5 (2)	O25—W8—O31	160.86 (19)
O38—W7—W8	84.21 (15)	O31—W8—W7	81.90 (14)
O38—W7—O3	74.61 (18)	O31—W8—O3	73.70 (18)
O38—W7—O18	90.5 (2)	O10—W9—O4	88.32 (18)
O38—W7—O23	90.4 (2)	O10—W9—O18	86.18 (19)
O38—W7—O32	160.33 (19)	O9—W8—O3	87.13 (18)
O3—W8—W7	41.62 (12)	O9—W8—O31	86.37 (18)
O9—W8—W7	128.68 (14)	O11—W8—W7	132.05 (16)
Compound 3			
Ni1—N4	2.059 (12)	W6—O2	2.341 (17)
Ni1—N6^{i}	2.075 (11)	W6—O3	1.907 (16)
Ni1—O1W	2.122 (10)	W6—O16	2.017 (15)
Ni1—O5W	2.087 (10)	W6—O19	1.697 (12)
Ni1—O6W	2.090 (10)	W6—O21	2.303 (19)
Ni1—O10	2.062 (9)	W6—O22	2.148 (17)

W1—O2	2.263 (16)	W1—O9	2.09 (3)
W1—O4	2.326 (16)	W1—O11^{ii}	1.832 (19)
W1—O5	1.686 (14)	W1—O13	1.873 (12)
W1—O18	1.992 (13)	W2—O8	1.94 (3)
W2—O4	2.316 (17)	W2—O9	2.12 (3)
W2—O6	2.237 (17)	W2—O14	1.937 (13)
W2—O7	1.689 (14)	W2—O20	2.022 (14)
W3—O2^{ii}	2.135 (17)	W3—O6	2.118 (17)
W3—O3^{ii}	2.035 (13)	W3—O10	1.737 (9)
W3—O15	1.829 (13)	W3—O11	1.750 (19)
W3—O20	2.068 (15)	W4—O1	1.687 (9)
W4—O8^{ii}	2.16 (3)	W4—O4^{ii}	2.389 (16)
W4—O12	2.022 (14)	W4—O16	2.095 (14)
W4—O18^{ii}	1.932 (14)	O2—O11^{ii}	1.80 (2)
W4—O21	2.211 (16)	W5—O15	1.961 (13)
W5—O12	1.998 (14)	W5—O17	1.615 (9)
W5—O14	2.134 (14)	W5—O21	2.301 (17)
W5—O22	1.916 (13)	O3—W6—O2	68.4 (6)
N4—Ni1—N6^{i}	95.2 (5)	O3—W6—O16	103.2 (7)
N4—Ni1—O1W	91.2 (4)	O3—W6—O21	111.3 (7)
N4—Ni1—O5W	91.0 (5)	O3—W6—O22	175.8 (7)
N4—Ni1—O6W	91.9 (5)	O16—W6—O2	114.3 (7)
N4—Ni1—O10	173.5 (5)	O16—W6—O21	69.0 (6)
N6^{i}—Ni1—O1W	91.9 (4)	O16—W6—O22	80.9 (6)
N6^{i}—Ni1—O5W	173.8 (5)	O19—W6—O2	152.5 (7)
N6^{i}—Ni1—O6W	91.0 (5)	O19—W6—O3	94.9 (7)
O5W—Ni1—O1W	87.7 (5)	O19—W6—O16	90.1 (6)
O5W—Ni1—O6W	89.1 (5)	O19—W6—O21	149.2 (7)
O6W—Ni1—O1W	175.6 (4)	O19—W6—O22	86.2 (6)
O10—Ni1—N6^{i}	89.9 (4)	O21—W6—O2	57.3 (6)
O10—Ni1—O1W	84.5 (4)	O22—W6—O2	109.0 (7)
O10—Ni1—O5W	83.9 (4)	O22—W6—O21	68.9 (6)
O10—Ni1—O6W	92.1 (4)	O5—W1—O11^{ii}	110.0 (8)
O2—W1—O4	50.3 (6)	O9—W1—O2	113.5 (10)
O5—W1—O2	150.0 (6)	O9—W1—O4	74.0 (10)
O5—W1—O4	159.7 (6)	O11^{ii}—W1—O2	50.7 (7)
O13—W1—O2	72.4 (6)	O11^{ii}—W1—O4	85.4 (7)
O13—W1—O4	106.0 (6)	O18—W1—O2	100.9 (6)
O13—W1—O9	95.4 (9)	O18—W1—O4	68.1 (6)
O13—W1—O18	173.2 (6)	O18—W1—O9	86.2 (10)
O7—W2—O14	84.7 (6)	O6—W2—O4	52.0 (6)
O7—W2—O20	88.5 (7)	O7—W2—O4	159.8 (7)

O8—W2—O4	75.8 (10)	O7—W2—O6	147.7 (7)
O8—W2—O6	111.7 (10)	O7—W2—O8	92.9 (10)
O8—W2—O20	95.0 (11)	O9—W2—O4	73.7 (10)
O20—W2—O4	109.0 (6)	O9—W2—O6	113.0 (10)
O20—W2—O6	69.6 (6)	O14—W2—O4	105.4 (6)
O3^{ii}—W3—O2^{ii}	70.7 (6)	O14—W2—O6	71.7 (6)
O3^{ii}—W3—O6	105.5 (6)	O14—W2—O8	175.8 (11)
O3^{ii}—W3—O20	86.5 (5)	O14—W2—O20	88.4 (6)
O6—W3—O2^{ii}	54.1 (6)	O15—W3—O2^{ii}	96.0 (6)
O10—W3—O2^{ii}	149.8 (5)	O15—W3—O3^{ii}	166.6 (6)
O10—W3—O3^{ii}	88.1 (5)	O15—W3—O3'^{ii}	147.3 (10)
O10—W3—O6	155.9 (6)	O15—W3—O6	64.1 (6)
O10—W3—O11	106.0 (7)	O15—W3—O20	97.3 (6)
O10—W3—O15	104.6 (5)	O20—W3—O2^{ii}	108.9 (6)
O10—W3—O20	90.3 (5)	O20—W3—O6	71.2 (6)
O11—W3—O2^{ii}	54.0 (7)	O8^{ii}—W4—O4^{ii}	70.4 (9)
O11—W3—O3^{ii}	88.6 (7)	O8^{ii}—W4—O21	107.5 (9)
O11—W3—O6	94.3 (7)	O12—W4—O4^{ii}	111.2 (6)
O11—W3—O15	84.0 (7)	O12—W4—O8^{ii}	176.5 (10)
O11—W3—O20	162.8 (7)	O12—W4—O16	82.3 (6)
O1—W4—O4^{ii}	156.1 (5)	O12—W4—O21	71.9 (6)
O1—W4—O8^{ii}	90.7 (9)	O16—W4—O4^{ii}	108.0 (6)
O1—W4—O12	88.6 (5)	O16—W4—O8^{ii}	94.3 (10)
O1—W4—O16	87.4 (5)	O16—W4—O21	69.5 (6)
O1—W4—O18^{ii}	96.6 (5)	W1—O2—W6	98.3 (6)
O1—W4—O21	151.1 (6)	W3^{ii}—O2—W1	103.5 (7)
O18^{ii}—W4—O21	107.3 (6)	W3^{ii}—O2—W6	99.6 (7)
O21—W4—O4^{ii}	52.4 (6)	O11^{ii}—O2—W1	52.1 (7)
O12—W5—O14	168.5 (6)	O11^{ii}—O2—W3^{ii}	52.0 (7)
O12—W5—O21	70.4 (6)	O11^{ii}—O2—W6	111.1 (9)
O14—W5—O21	105.9 (6)	W6—O3—W3^{ii}	120.4 (7)
O15—W5—O12	85.2 (6)	W1—O4—W4^{ii}	96.6 (6)
O15—W5—O14	83.8 (6)	W2—O4—W1	98.7 (6)
O15—W5—O21	88.9 (6)	W2—O4—W4^{ii}	96.1 (6)
O17—W5—O12	94.6 (6)	W3—O6—W2	104.5 (7)
O17—W5—O14	91.1 (5)	W2—O8—W4^{ii}	117.0 (15)
O17—W5—O15	102.1 (5)	W1—O9—W2	113.5 (15)
O17—W5—O21	160.8 (5)	W3—O10—Ni1	151.3 (6)
O17—W5—O22	95.7 (5)	W3—O11—W1^{ii}	149.4 (11)
O22—W5—O12	89.0 (6)	W3—O11—O2^{ii}	74.0 (9)
O22—W5—O14	100.4 (6)	O2^{ii}—O11—W1^{ii}	77.1 (9)

O22—W5—O15	161.7 (6)	W5—O12—W4	117.9 (7)
O22—W5—O21	72.8 (6)	W2—O20—W3	114.7 (7)
W2—O14—W5	125.2 (7)	W4—O21—W5	99.5 (7)
W3—O15—W5	140.9 (7)	W4—O21—W6	102.3 (6)
W6—O16—W4	117.5 (7)	W5—O21—W6	99.0 (7)
W4^{ii}—O18—W1	127.5 (7)	W5—O22—W6	118.9 (7)

Symmetry codes: **(1)**: (i) *y*−1/2, −*z*+3/2, −*x*+1; (ii) −*z*+1, *x*+1/2, −*y*+3/2; (iii) *z*, −*x*+3/2, *y*−1/2; (iv) *z*, *x*, *y*; (v) −*z*+1, −*x*+1, −*y*+1; (vi) −*x*+1, −*y*+1, −*z*+1; (vii) *y*, *z*, *x*; (viii) −*y*+1, −*z*+1, −*x*+1; (ix) −*x*+1, −*y*+2, −*z*+1; (x) −*y*+3/2, *z*+1/2, *x*; (xi) −*z*+1/2, −*x*+1, *y*−1/2; (xii) −*y*+1, *z*+1/2, −*x*+1/2.

(2): (i) *x*+1/2, *y*−1/2, *z*; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) −*x*+1, *y*, −*z*+1/2; (iv) *x*, *y*−1, *z*; (v) *x*−1/2, *y*+1/2, *z*; (vi) *x*, *y*+1, *z*. **(3)** (i) −*x*, −*y*, −*z*−1; (ii) −*x*, −*y*−2, −*z*−2.