Electronic supplementary information

Zinc and copper coordination polymers with 4,4′-bipyridine and 2-sulfoterephthalate: infinite polypseudorotaxane and unprecedented (3,4,4)-connected trinodal topology

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Experimental section.

General information. Solvents were dried with standard procedures. Starting chemicals were purchased from commercial source and used as received. Elemental analysis was performed on a Thermo Flash 2000 CHN-O elemental analyzer. Thermogravimetric analysis was performed on a Perkin-Elmer Pyris 6 Thermogravimetric Analyzer under flowing N_2 gas (80 mL/min), and the heating rate was 20 °C/min. Powder X-ray diffraction (PXRD) measurements were recorded on Shimadzu Lab-X XRD-6000 diffractometer with Cu Kα, λ = 1.54060 Å.

Synthesis of $\{[Zn(2\text{-stp})(bpy)(H_2O)(H_2O)_{0.25}]_2[Zn(bipy)(H_2O)_4]\cdot 4H_2O\}_n$ (1).

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2975 g, 1.0 mmol), 2-sulfoterephthalic acid monosodium salt (0.0536 g, 0.20 mmol), and 4,4'-bipyridyl (0.2191 g, 1.4 mmol) in water (4 mL) was heated to 160 °C for 48 h. Then it was allowed to cool down to room temperature at the rate −6°C/h. Yellowish crystals were separated by filtration, washed with deionized water, and dried in air. Yield: 0.128 g, 96 % based on 2-stpH_3. Anal. Calc. for $C_{46}H_{43}N_6O_{20.5}S_2Zn_3 \cdot 4H_2O$: C, 41.22; H, 3.84; N, 6.27. Found: C, 41.00; H, 3.80; N, 6.19. IR data (KBr, cm^{-1}): 1601, 1528, 1477, 1393, 1385, 1354, 1188, 1157, 1072, 1022, 822, 806, 783, 729, 679, 621, 571, 505, 482, 463.

Synthesis of $\{Cu_3(2\text{-stp})_2(bpy)(H_2O)_4\}_n$ (2). A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.121 g, 0.50 mmol), 2-sulfoterephthalic acid monosodium salt (0.0536 g, 0.20 mmol), and 4,4'-bipyridine (0.0626 g, 0.40 mmol) in water (4 mL) was heated under the same condition above. Blue-block crystals were obtained. Yield: 0.071 g, 84% based on 2-stpH_3. Anal. Calc. for $C_{26}H_{22}Cu_3N_2O_{18}S_2$: C, 34.50; H, 2.45; N, 3.09. Found : C, 34.56; H, 2.40; N, 3.00. IR data (KBr, cm^{-1}): 1609, 1574, 1543, 1485, 1416, 1381, 1219, 1196, 1161, 1076, 1026, 934, 883, 845, 814, 783, 725, 691, 633, 625, 571, 513, 501, 462, 451.

X-ray crystallographic studies. Reflection data were collected on a Bruker APEX II equipped with a CCD area detector and a graphite monochromater utilizing Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. The unit cell parameters were obtained

by least-squares refinement. The data were integrated via SAINT.[1] Lorentz and polarization effect and multiscan absorption corrections were applied with SADABS.[2] The structures were solved by direct methods and refined by full-matrix least squares methods against F^2 with SHELXTL.[3] All non-H atoms were refined anisotropically. All H-atoms, except those of water, were fixed at calculated positions and refined with the use of a riding model. H-atoms in water were located in the electron density map and not refined. Crystallographic data are listed in Table 1S. Selected bond distances and angles are listed in Table S2 and S3. CCDC-795271 (**1**) and -795272 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

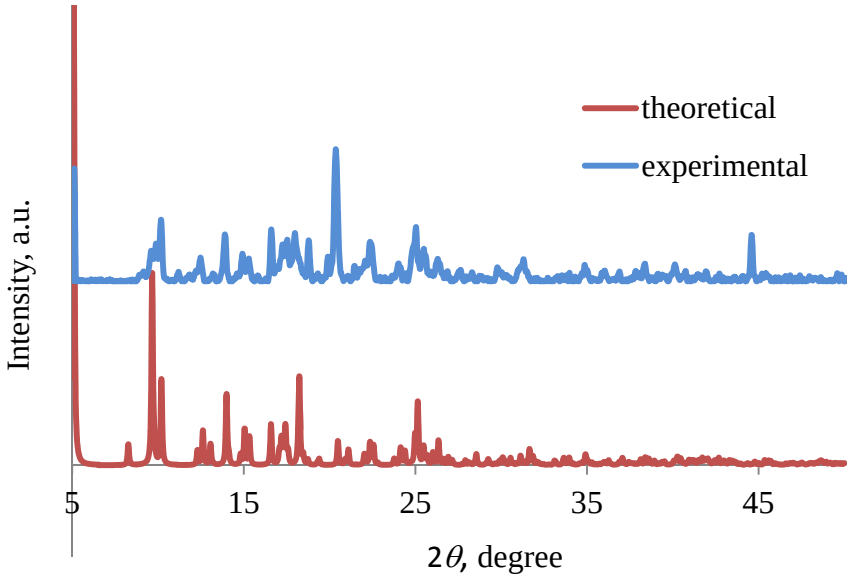

Figure S1. The PXRD pattern of **1**.

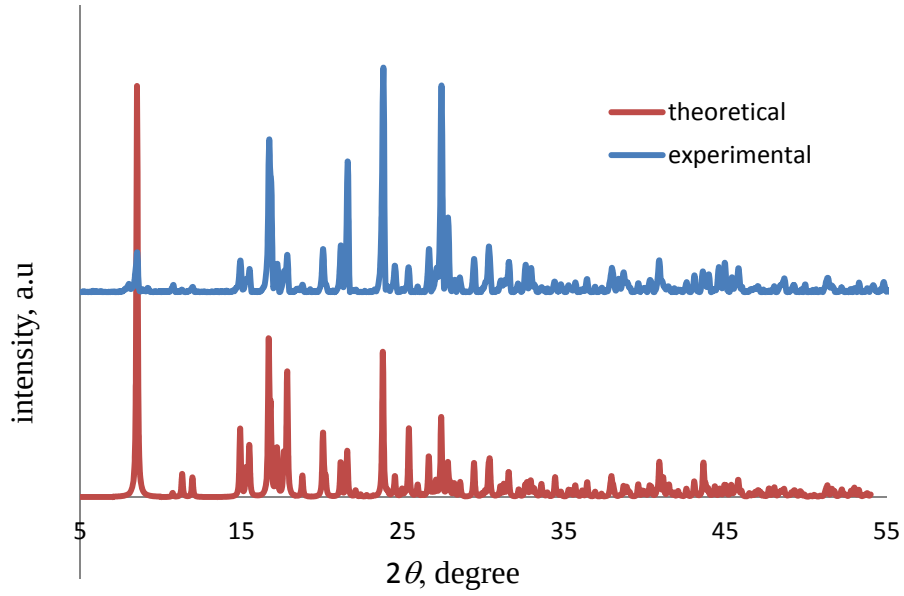

Figure S2. The PXRD pattern of **2**.

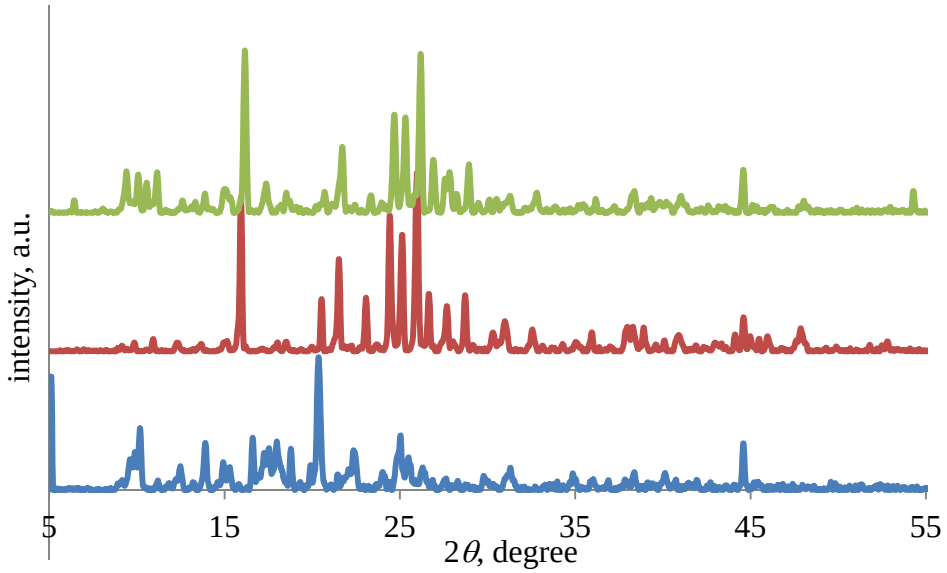

Figure S3. The PXRD patterns of samples obtained from a mixture of $Zn(NO_3)_2 \cdot 6H_2O$, 2-stpH_2Na, and bpy in a mole ratio of 5:1:7 (lower trace, pure **1**), 1:1:1 (middle trace), and 3:2:3 (upper trace).

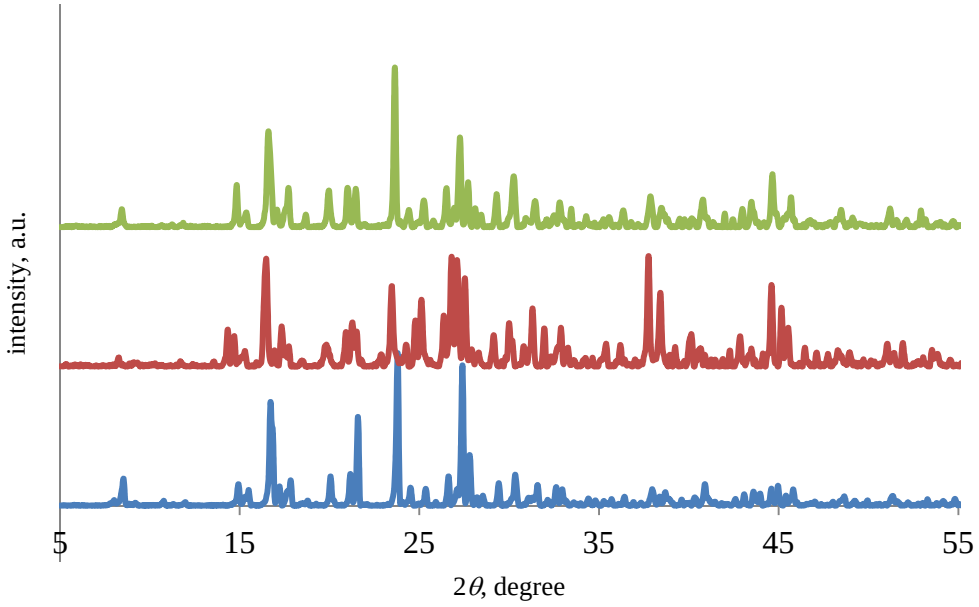

Figure S4. The PXRD patterns of samples obtained from a mixture of $Cu(NO_3)_2 \cdot 3H_2O$, 2-stpH_2Na, and bpy in a mole ratio of 5:1:7 (lower trace, pure **2**), 1:1:1 (middle trace), and 3:2:1 (upper trace).

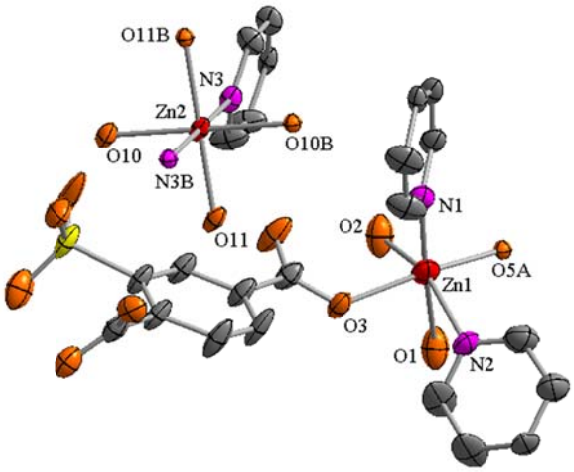

Figure S5. Coordination environment of **1** with thermal ellipsoids shown at 50% probability.

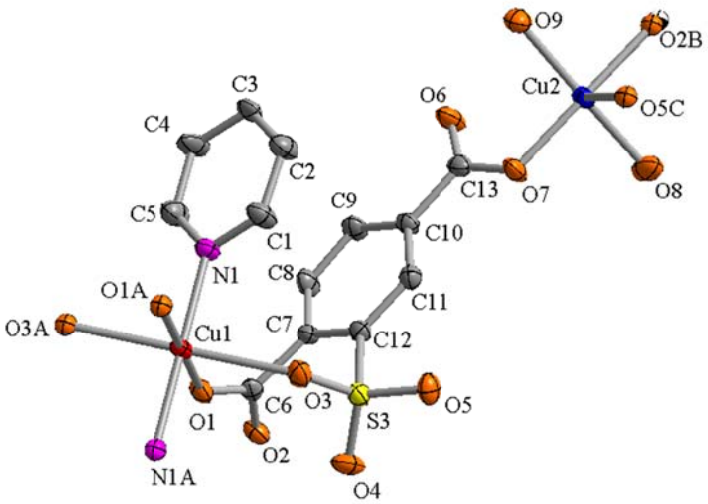

Figure S6. Coordination environment of **2** with thermal ellipsoids shown at 50% probability.

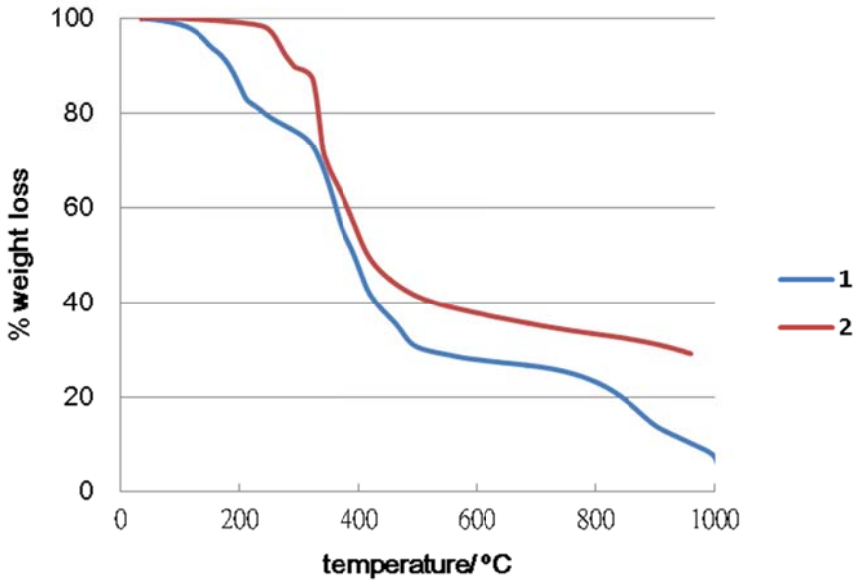

Figure S7. The TGA curves of **1** and **2**.

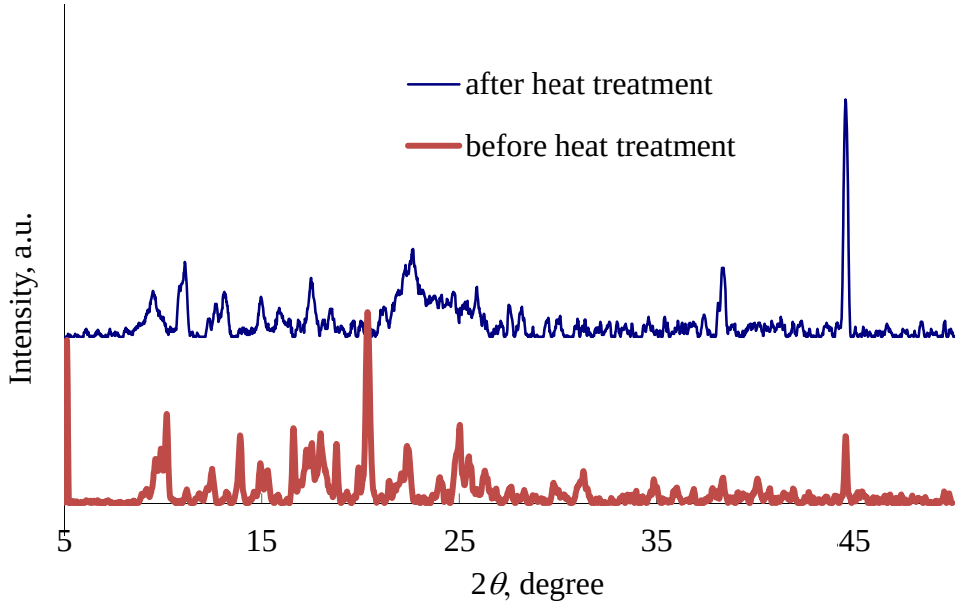

Figure S8. The PXRD pattern of **1** before and after heat treatment.

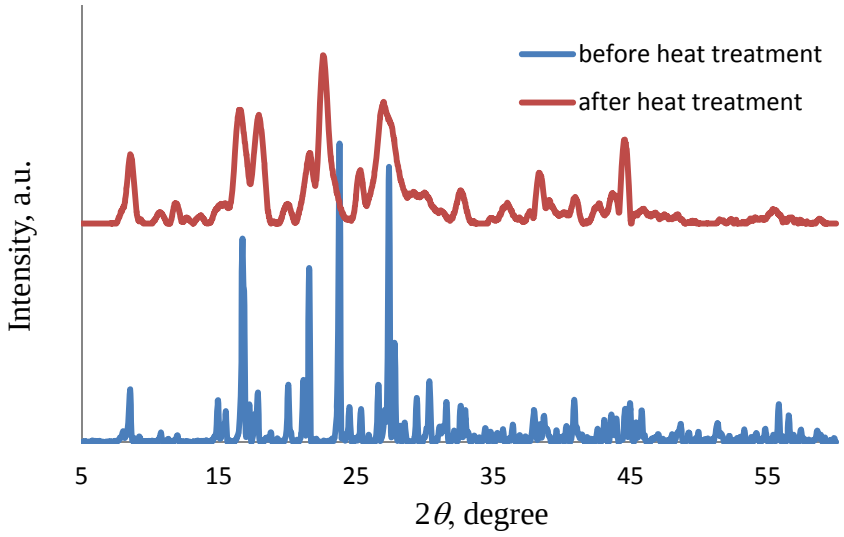

Figure S9. The PXRD pattern of **2** before and after heat treatment.

Table S1. Selected bond distances and angles in **1** (Å and º)

Zn1–O1	2.37(3)	O1–Zn1–N2	79.4(5)	N1–Zn1–O1	174.7(5)
Zn1–O2	2.058(5)	O1–Zn1–O3,	92.6(4)	O3–Zn1–O5A	163.97(17)
Zn1–O3	2.084(4)	O1–Zn1–O5A	73.1(4)	O2–Zn1–N2	153.0(2)
Zn1–O5A	2.049(4)	O1–Zn1–O2	74.7(5)	O10–Zn2–O11	89.44(13)
Zn1–N1	2.083(5)	N1–Zn1–O2	102.40(19)	O11–Zn2–N3B	91.63(14)
Zn1–N2	2.088(4)	N1–Zn1–O3	91.60(17)	O11–Zn2–O10B	90.56(13)
Zn2–O10	2.134(3)	N1–Zn1–O5A	102.33(17)	O11–Zn2–N3	88.37(14)
Zn2–O11	2.067(3)	N1–Zn1–N2	104.0(2)	O11–Zn2–O11B	180.000(1)
Zn2–N3	2.169(4)	O3–Zn1–N2	87.72(16)	O10–Zn2–O10B	179.999(1)
		O2–Zn1–O3	86.29(16)	N3–Zn2–N3B	180.00(19)
		O2–Zn1–O5A	83.03(16)	O10–Zn2–N3B	90.13(14)
		N2–Zn1–O5A	96.42(17)	O10–Zn2–N3	89.86(14)

symmetry code: A, x, y+1, z; B, -x +1, -y,-1, -z+1

Table S2. Selected bond distances and angles in **2** (Å and º)

Cu1–N1	1.972(4)	O1–Cu1–N1A,	85.66(13)	O7–Cu2–O8,	89.91(13)
Cu1–O1	2.065(3)	O1–Cu1–O3A,	89.69(10)	O8–Cu2–O2B,	87.46(13)

Cu1–O3	2.284(3)	O1–Cu1–O3,	90.31(10)	O9–Cu2–O2B	89.66(13)
Cu2–O5C	2.300(3)	O1–Cu1–N1,	94.34(13)	O5C–Cu2–O7	92.32(12)
Cu1–O7	1.928(3)	O3–Cu1–N1,	91.77(12)	O5C–Cu2–O8	98.65(12)
Cu1–O8	1.973(3)	O3–Cu1–N1A,	88.23(12)	O5C–Cu2–O2B	94.48(11)
Cu1–O9	1.979(3)	N1–Cu1–N1A,	179.999(1)	O5C–Cu2–O9	86.95(11)
Cu2–O2B	1.988(3)	O3–Cu1–O3A,	180.0	O8–Cu2–O9	173.89(13)
		O1–Cu1–O1A,	180.00(18)	O2B–Cu2–O7	173.00(12)
		O7–Cu2–O9,	92.34(13)		

symmetry code A: -x, 2-y, -z; B: 1+x, 1.5-y, 0.5+z; C: 1-x, 2-y, 1-z

Table S3. Hydrogen bonding geometry in **1** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(10)-H(10B)...O(8)	0.83	1.99	2.774(6)	157.2
O(11)-H(11B)...O(6)	0.95	1.70	2.627(5)	163.0
O(10)-H(10C)...O(9)#7	0.77	2.28	3.003(7)	155.5
O(11)-H(11A)...O(7)#8	0.78	2.51	3.158(5)	141.8
O(11)-H(11A)...O(9)#8	0.78	2.25	2.909(6)	143.2
C(1)-H(1A)...O(3)	0.95	2.48	2.99(2)	113.1
C(13)-H(13A)...O(9)	0.95	2.45	2.850(6)	105.4
C(23)-H(23A)...O(11)	0.95	2.42	2.995(6)	119.0
C(2)-H(2A)...O(3)#9	0.95	2.57	3.42(3)	149.3
C(5)-H(5A)...O(6)#5	0.95	2.59	3.467(7)	154.3
C(7)-H(7A)...O(9)#8	0.95	2.47	3.327(7)	149.3
C(10)-H(10A)...O(8)#5	0.95	2.34	3.260(7)	163.4
C(19)-H(19A)...O(6)#6	0.95	2.43	3.379(7)	172.7
C(19)-H(19A)...O(11)#6	0.95	2.58	3.131(6)	117.1
C(20)-H(20A)...O(4)#3	0.95	2.38	3.289(7)	159.9

Symmetry transformations used to generate equivalent atoms:
#1 -x+2, -y, -z #2 -x+1, -y, -z+1 #3 -x, -y, -z+1
#4 x, y-1, z #5 x, y+1, z #6 -x+1, -y-1, -z+1 #7 -x, -y-1, -z+1
#8 x+1, y, z #9 -x+1, -y, -z

Table S4. Hydrogen bonding geometry of **2** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8A)...O(4)#3	0.84	2.01	2.835(4)	166.3
O(8)-H(8B)...O(6)#6	0.74	2.07	2.734(4)	150.7
O(9)-H(9A)...O(4)#7	0.84	2.03	2.867(4)	174.4
O(9)-H(9B)...O(2)#8	0.91	1.90	2.778(4)	161.4
C(1)-H(1)...O(3)	0.95	2.47	3.028(6)	117.6
C(11)-H(11)...O(5)	0.95	2.52	2.914(5)	105.2
C(1)-H(1)...O(6)#8	0.95	2.44	3.109(5)	127.6
C(5)-H(5)...O(3)#2	0.95	2.54	3.030(6)	112.4
C(8)-H(8)...O(5)#9	0.95	2.30	3.247(5)	175.8

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+2, -z #2 -x, -y+2, -z #3 x+1, -y+3/2, z+1/2
#4 -x+1, -y+2, -z+1 #5 x-1, -y+3/2, z-1/2 #6 x, -y+3/2, z+1/2
#7 x+1, y, z #8 -x+1, y+1/2, -z+1/2 #9 x, -y+3/2, z-1/2

References

1. *SAINT*, Bruker AXS Inc.:Madison, Wisconsin, USA., 2007.

2. Sheldrick, G. M. *SADABS*, University of Göttingen, Germany, 1996.

3. Sheldrick, G. *Acta Crystallogr.* **2008,** *A64*, 112.