Electronic Supplementary Material (ESI) for RSC Advances.

Two novel hybrid polyoxometalates constructed from Preyssler P_5W_{30} clusters and Schiff base exhibiting interesting third-order NLO properties

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1. PXRD patterns

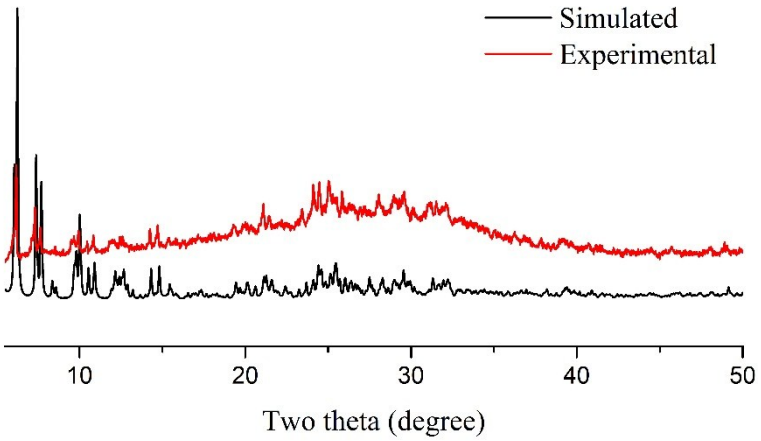

Fig. S1 The simulative (black) and experimental (red) powder X-ray diffraction patterns for compound **1.**

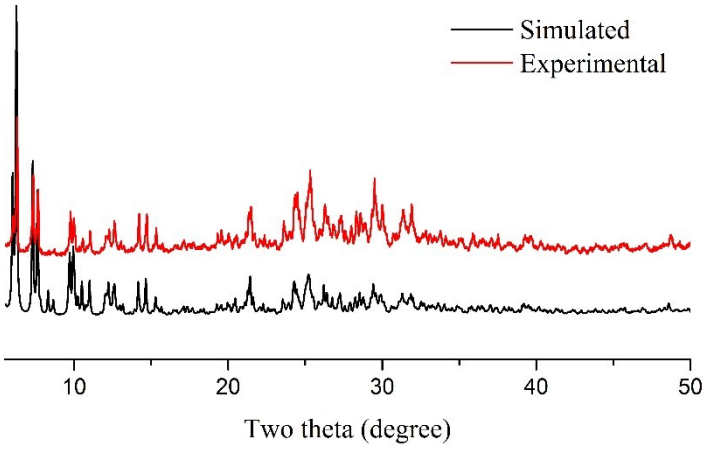

Fig. S2 The simulative (black) and experimental (red) powder X-ray diffraction

patterns for compound **2.**

2. IR spectra

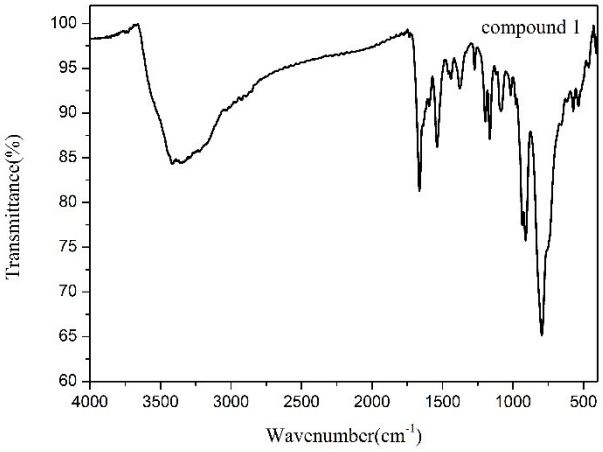

Fig. S3 The IR spectra of compound **1.**

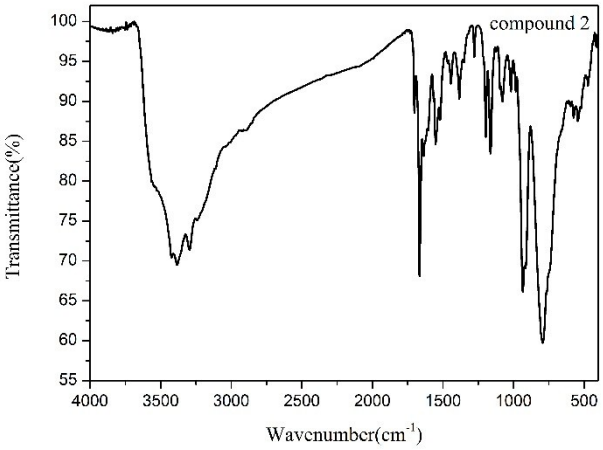

Fig. S4 The IR spectra of compound **2.**

3. The TG curves for 1 and 2

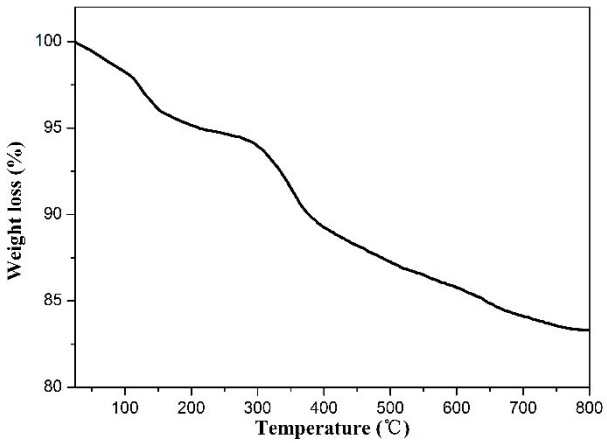

Fig. S5 The TG curve of compound **1**.

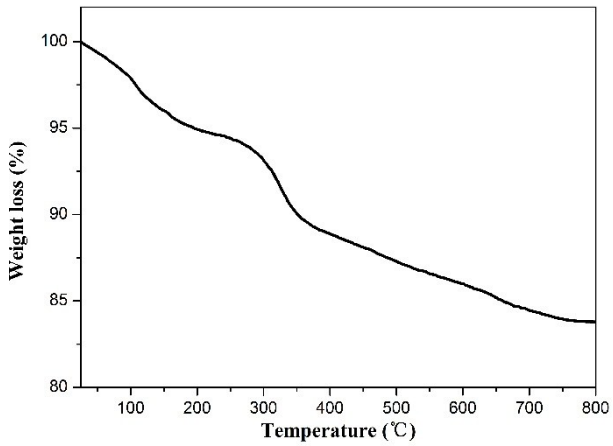

Fig. S6 The TG curve of compound **2**.

4. Microscope images

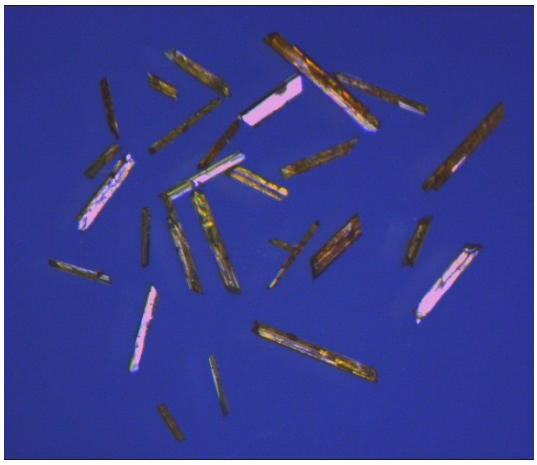

Fig. S7 Microscope image of compound **1.**

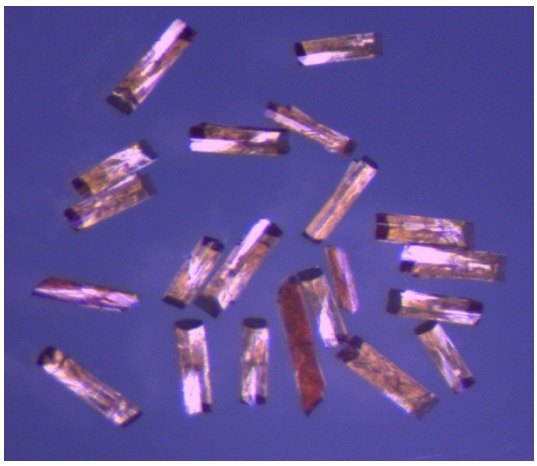

Fig. S8 Microscope image of compound **2.**

5. The coordination modes of Transition Metal ions

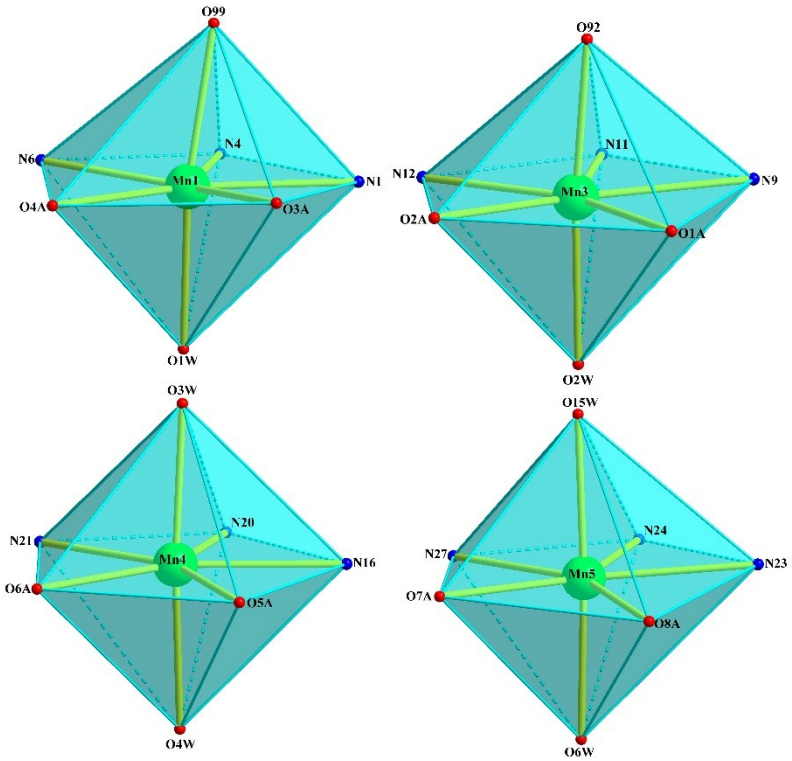

Fig. S9 The coordination modes of Mn ion in compound **1.**

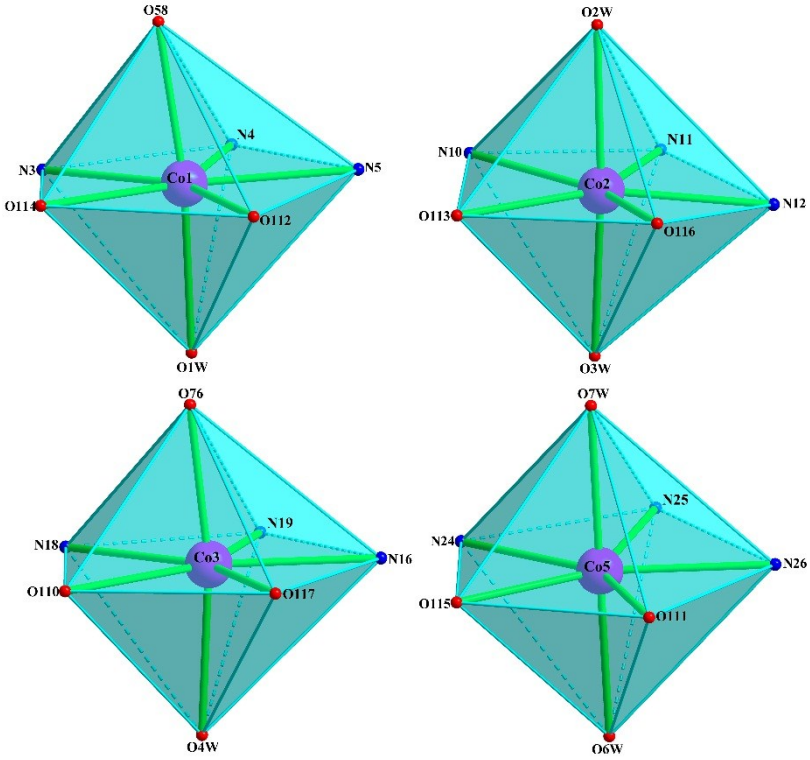

Fig. S10 The coordination modes of Co ion in compound **2.**

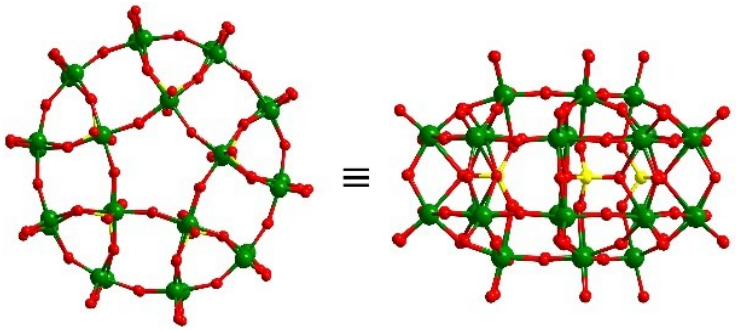

Fig. S11 Ball-and-stick representation of Preyssler-type P_5W_{30} anion.

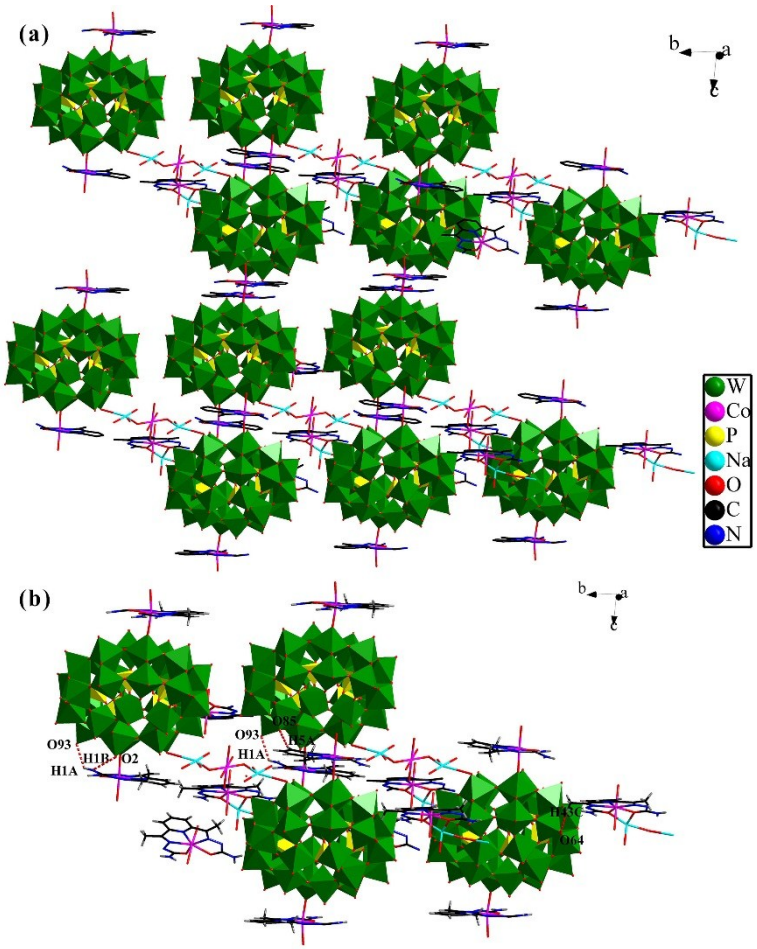

Fig. S12 (a) Polyhedral and stick representation of the 3D framework of compound **2**, (b) Hydrogen bonds interactions between adjacent clusters of compound **2**.

6. Bond Valence Sum Calculations

Table S1. Selected bond valence sum (BVS) values for compounds **1** (left) and **2** (right).

Mn	**BVS value**	**Co**	**BVS value**

Mn1	2.22	Co1	2.21
Mn2	2.02	Co2	2.39
Mn3	2.25	Co3	2.36
Mn4	2.28	Co4	1.80
Mn5	2.19	Co5	2.25

7. Selected bond lengths and angles

Table S2. Selected bond lengths (Å) and bond angles (°) for compound **1.**

Mn(1)-O(1W)	2.213(16)	Mn(3)-O(1A)	2.27(2)
Mn(1)-O(99)	2.216(15)	Mn(3)-N(12)	2.319(18)
Mn(1)-O(3A)	2.222(16)	Mn(3)-N(9)	2.323(19)
Mn(1)-O(4A)	2.241(15)	Mn(4)-O(6A)	2.156(17)
Mn(1)-N(6)	2.272(17)	Mn(4)-O(5A)	2.22(2)
Mn(1)-N(4)	2.275(19)	Mn(4)-O(3W)	2.22(2)
Mn(1)-N(1)	2.280(16)	Mn(4)-O(4W)	2.252(19)
Mn(2)-O(7W)	2.171(19)	Mn(4)-N(16)	2.275(17)
Mn(2)-O(7W)#1	2.171(19)	Mn(4)-N(20)	2.278(18)
Mn(2)-O(13W)#1	2.204(5)	Mn(4)-N(21)	2.296(19)
Mn(2)-O(13W)	2.204(5)	Mn(5)-O(6W)	2.20(2)
Mn(2)-O(12W)#1	2.205(5)	Mn(5)-O(7A)	2.217(18)
Mn(2)-O(12W)	2.205(5)	Mn(5)-O(8A)	2.223(18)
Mn(3)-O(92)	2.129(16)	Mn(5)-N(24)	2.25(2)
Mn(3)-O(2W)	2.16(2)	Mn(5)-O(15W)	2.25(2)
Mn(3)-O(2A)	2.26(2)	Mn(5)-N(27)	2.306(19)
Mn(3)-N(11)	2.27(2)	Mn(5)-N(23)	2.33(2)
O(1W)-Mn(1)-O(99)	171.6(6)	O(2W)-Mn(3)-O(1A)	88.0(8)
O(1W)-Mn(1)-O(3A)	98.6(7)	O(2A)-Mn(3)-O(1A)	85.3(7)
O(99)-Mn(1)-O(3A)	81.4(6)	N(11)-Mn(3)-O(1A)	139.0(7)
O(1W)-Mn(1)-O(4A)	91.6(6)	O(92)-Mn(3)-N(12)	97.7(7)
O(99)-Mn(1)-O(4A)	96.7(6)	O(2W)-Mn(3)-N(12)	90.8(8)
O(3A)-Mn(1)-O(4A)	83.4(6)	O(2A)-Mn(3)-N(12)	69.9(7)
O(1W)-Mn(1)-N(6)	89.4(7)	N(11)-Mn(3)-N(12)	65.9(7)
O(99)-Mn(1)-N(6)	94.4(6)	O(1A)-Mn(3)-N(12)	155.1(8)
O(3A)-Mn(1)-N(6)	152.8(6)	O(92)-Mn(3)-N(9)	84.4(6)
O(4A)-Mn(1)-N(6)	70.3(6)	O(2W)-Mn(3)-N(9)	92.7(7)
O(1W)-Mn(1)-N(4)	85.6(7)	O(2A)-Mn(3)-N(9)	155.9(7)
O(99)-Mn(1)-N(4)	88.7(6)	N(11)-Mn(3)-N(9)	68.0(7)
O(3A)-Mn(1)-N(4)	137.5(6)	O(1A)-Mn(3)-N(9)	71.0(7)
O(4A)-Mn(1)-N(4)	139.0(6)	N(12)-Mn(3)-N(9)	133.9(8)

N(6)-Mn(1)-N(4)	68.8(6)	O(6A)-Mn(4)-O(5A)	80.5(7)
O(1W)-Mn(1)-N(1)	90.2(6)	O(6A)-Mn(4)-O(3W)	94.2(9)
O(99)-Mn(1)-N(1)	81.9(6)	O(5A)-Mn(4)-O(3W)	91.1(9)
O(3A)-Mn(1)-N(1)	70.2(6)	O(6A)-Mn(4)-O(4W)	90.9(8)
O(4A)-Mn(1)-N(1)	153.5(6)	O(5A)-Mn(4)-O(4W)	90.4(8)
N(6)-Mn(1)-N(1)	136.1(7)	O(3W)-Mn(4)-O(4W)	174.8(8)
N(4)-Mn(1)-N(1)	67.4(6)	O(6A)-Mn(4)-N(16)	151.4(8)
O(7W)-Mn(2)-O(7W)#1	180	O(5A)-Mn(4)-N(16)	70.9(7)
O(7W)-Mn(2)-O(13W)#1	85.9(10)	O(3W)-Mn(4)-N(16)	88.0(8)
O(7W)#1-Mn(2)-O(13W)#1	94.1(10)	O(4W)-Mn(4)-N(16)	87.8(6)
O(7W)-Mn(2)-O(13W)	94.1(10)	O(6A)-Mn(4)-N(20)	138.9(7)
O(7W)#1-Mn(2)-O(13W)	85.9(10)	O(5A)-Mn(4)-N(20)	140.2(7)
O(13W)#1-Mn(2)-O(13W)	180	O(3W)-Mn(4)-N(20)	90.6(9)
O(7W)-Mn(2)-O(12W)#1	87.0(10)	O(4W)-Mn(4)-N(20)	85.1(7)
O(7W)#1-Mn(2)-O(12W)#1	93.0(10)	N(16)-Mn(4)-N(20)	69.5(7)
O(13W)#1-Mn(2)-O(12W)#1	112.2(15)	O(6A)-Mn(4)-N(21)	70.5(7)
O(13W)-Mn(2)-O(12W)#1	67.8(15)	O(5A)-Mn(4)-N(21)	151.0(7)
O(7W)-Mn(2)-O(12W)	93.0(10)	O(3W)-Mn(4)-N(21)	92.5(9)
O(7W)#1-Mn(2)-O(12W)	87.0(10)	O(4W)-Mn(4)-N(21)	88.6(7)
O(13W)#1-Mn(2)-O(12W)	67.8(15)	N(16)-Mn(4)-N(21)	138.0(7)
O(13W)-Mn(2)-O(12W)	112.2(15)	N(20)-Mn(4)-N(21)	68.5(7)
O(12W)#1-Mn(2)-O(12W)	180	O(6W)-Mn(5)-O(7A)	88.9(7)
O(7W)-Mn(2)-Na(3)#1	90.0(6)	O(6W)-Mn(5)-O(8A)	86.8(8)
O(7W)#1-Mn(2)-Na(3)#1	90.0(6)	O(7A)-Mn(5)-O(8A)	83.5(7)
O(13W)#1-Mn(2)-Na(3)#1	144.6(11)	O(6W)-Mn(5)-N(24)	91.8(8)
O(13W)-Mn(2)-Na(3)#1	35.4(11)	O(7A)-Mn(5)-N(24)	138.3(7)
O(12W)#1-Mn(2)-Na(3)#1	32.4(11)	O(8A)-Mn(5)-N(24)	138.2(8)
O(12W)-Mn(2)-Na(3)#1	147.6(11)	O(6W)-Mn(5)-O(15W)	177.0(8)
O(7W)-Mn(2)-Na(3)	90.0(6)	O(7A)-Mn(5)-O(15W)	88.3(8)
O(7W)#1-Mn(2)-Na(3)	90.0(6)	O(8A)-Mn(5)-O(15W)	93.9(8)
O(13W)#1-Mn(2)-Na(3)	35.4(11)	N(24)-Mn(5)-O(15W)	89.6(8)
O(13W)-Mn(2)-Na(3)	144.6(11)	O(6W)-Mn(5)-N(27)	88.3(7)
O(12W)#1-Mn(2)-Na(3)	147.6(11)	O(7A)-Mn(5)-N(27)	70.6(7)
O(12W)-Mn(2)-Na(3)	32.4(11)	O(8A)-Mn(5)-N(27)	153.7(7)
Na(3)#1-Mn(2)-Na(3)	180	N(24)-Mn(5)-N(27)	67.7(7)
O(92)-Mn(3)-O(2W)	170.6(8)	O(15W)-Mn(5)-N(27)	89.8(8)
O(92)-Mn(3)-O(2A)	88.7(7)	O(6W)-Mn(5)-N(23)	95.6(7)
O(2W)-Mn(3)-O(2A)	90.4(8)	O(7A)-Mn(5)-N(23)	151.9(8)
O(92)-Mn(3)-N(11)	94.0(7)	O(8A)-Mn(5)-N(23)	69.1(8)
O(2W)-Mn(3)-N(11)	93.1(9)	N(24)-Mn(5)-N(23)	69.4(8)
O(2A)-Mn(3)-N(11)	135.7(7)	O(15W)-Mn(5)-N(23)	87.4(8)
O(92)-Mn(3)-O(1A)	82.6(7)	N(27)-Mn(5)-N(23)	137.1(8)

Symmetry transformations used to generate equivalent atoms: #1 –x-2,-y+2,-z+2.

Table S3. Selected bond lengths (Å) and bond angles (°) for compound **2.**

Co(1)-O(58)	2.114(16)	Co(3)-N(19)	2.16(3)
Co(1)-O(1W)	2.19(2)	Co(3)-O(110)	2.20(3)
Co(1)-O(112)	2.19(2)	Co(3)-N(18)	2.20(3)
Co(1)-N(3)	2.19(2)	Co(3)-O(117)	2.22(2)
Co(1)-N(4)	2.21(2)	Co(4)-O(27W)#1	1.99(3)
Co(1)-N(5)	2.21(2)	Co(4)-O(27W)	1.99(3)
Co(1)-O(114)	2.24(2)	Co(4)-O(11W)#1	2.13(2)
Co(2)-O(3W)	2.15(2)	Co(4)-O(11W)	2.13(2)
Co(2)-O(113)	2.16(2)	Co(4)-O(30W)#1	2.40(5)
Co(2)-N(10)	2.16(2)	Co(4)-O(30W)	2.40(5)
Co(2)-O(2W)	2.17(2)	Co(5)-O(115)	2.14(2)
Co(2)-O(116)	2.17(2)	Co(5)-O(111)	2.16(2)
Co(2)-N(11)	2.17(3)	Co(5)-N(25)	2.17(2)
Co(2)-N(12)	2.17(2)	Co(5)-O(6W)	2.17(3)
Co(3)-O(76)	2.068(18)	Co(5)-O(7W)	2.18(2)
Co(3)-O(4W)	2.14(3)	Co(5)-N(26)	2.21(2)
Co(3)-N(16)	2.15(2)	Co(5)-N(24)	2.23(3)
O(58)-Co(1)-O(1W)	173.6(8)	O(76)-Co(3)-N(18)	87.8(8)
O(58)-Co(1)-O(112)	93.6(7)	O(4W)-Co(3)-N(18)	90.1(10)
O(1W)-Co(1)-O(112)	88.9(8)	N(16)-Co(3)-N(18)	140.5(10)
O(58)-Co(1)-N(3)	85.0(8)	N(19)-Co(3)-N(18)	71.4(10)
O(1W)-Co(1)-N(3)	89.7(9)	O(110)-Co(3)-N(18)	71.3(9)
O(112)-Co(1)-N(3)	148.5(8)	O(76)-Co(3)-O(117)	88.7(8)
O(58)-Co(1)-N(4)	91.2(7)	O(4W)-Co(3)-O(117)	87.1(10)
O(1W)-Co(1)-N(4)	90.5(8)	N(16)-Co(3)-O(117)	71.6(9)
O(112)-Co(1)-N(4)	140.8(7)	N(19)-Co(3)-O(117)	140.7(9)
N(3)-Co(1)-N(4)	70.6(8)	O(110)-Co(3)-O(117)	76.7(8)
O(58)-Co(1)-N(5)	94.9(7)	N(18)-Co(3)-O(117)	147.9(9)
O(1W)-Co(1)-N(5)	91.5(8)	O(27W)#1-Co(4)-O(27W)	179.999(15)
O(112)-Co(1)-N(5)	70.4(8)	O(27W)#1-Co(4)-O(11W)#1	87.7(12)
N(3)-Co(1)-N(5)	141.0(9)	O(27W)-Co(4)-O(11W)#1	92.3(12)
N(4)-Co(1)-N(5)	70.4(8)	O(27W)#1-Co(4)-O(11W)	92.3(12)
O(58)-Co(1)-O(114)	83.2(7)	O(27W)-Co(4)-O(11W)	87.7(12)
O(1W)-Co(1)-O(114)	91.7(8)	O(11W)#1-Co(4)-O(11W)	180
O(112)-Co(1)-O(114)	77.9(7)	O(11W)#1-Co(4)-O(30W)#1	85.0(14)
N(3)-Co(1)-O(114)	70.7(8)	O(11W)-Co(4)-O(30W)#1	95.0(14)
N(4)-Co(1)-O(114)	141.2(8)	O(11W)#1-Co(4)-O(30W)	95.0(14)
N(5)-Co(1)-O(114)	148.1(9)	O(11W)-Co(4)-O(30W)	85.0(14)
O(3W)-Co(2)-O(113)	87.9(8)	O(30W)#1-Co(4)-O(30W)	179.999(12)

O(3W)-Co(2)-N(10)	91.4(10)	O(11W)#1-Co(4)-Na(2)	89.9(8)
O(113)-Co(2)-N(10)	72.9(9)	O(11W)-Co(4)-Na(2)	90.1(8)
O(3W)-Co(2)-O(2W)	176.2(9)	O(30W)#1-Co(4)-Na(2)	87.4(15)
O(113)-Co(2)-O(2W)	88.3(9)	O(30W)-Co(4)-Na(2)	92.6(15)
N(10)-Co(2)-O(2W)	87.2(10)	O(11W)#1-Co(4)-Na(2)#1	90.1(8)
O(3W)-Co(2)-O(116)	94.0(9)	O(11W)-Co(4)-Na(2)#1	89.9(8)
O(113)-Co(2)-O(116)	75.8(8)	O(30W)#1-Co(4)-Na(2)#1	92.6(15)
N(10)-Co(2)-O(116)	148.0(10)	O(30W)-Co(4)-Na(2)#1	87.4(15)
O(2W)-Co(2)-O(116)	85.4(9)	Na(2)-Co(4)-Na(2)#1	180.0(7)
O(3W)-Co(2)-N(11)	90.2(9)	O(115)-Co(5)-O(111)	74.1(8)
O(113)-Co(2)-N(11)	143.1(9)	O(115)-Co(5)-N(25)	141.5(9)
N(10)-Co(2)-N(11)	70.3(10)	O(111)-Co(5)-N(25)	144.0(9)
O(2W)-Co(2)-N(11)	92.6(10)	O(115)-Co(5)-O(6W)	91.3(10)
O(116)-Co(2)-N(11)	141.0(9)	O(111)-Co(5)-O(6W)	89.6(10)
O(3W)-Co(2)-N(12)	87.3(8)	N(25)-Co(5)-O(6W)	94.1(11)
O(113)-Co(2)-N(12)	146.8(8)	O(115)-Co(5)-O(7W)	88.4(8)
N(10)-Co(2)-N(12)	140.1(10)	O(111)-Co(5)-O(7W)	88.9(8)
O(2W)-Co(2)-N(12)	96.0(8)	N(25)-Co(5)-O(7W)	87.0(9)
O(116)-Co(2)-N(12)	71.7(8)	O(6W)-Co(5)-O(7W)	178.5(10)
N(11)-Co(2)-N(12)	69.8(9)	O(115)-Co(5)-N(26)	145.6(8)
O(76)-Co(3)-O(4W)	168.4(10)	O(111)-Co(5)-N(26)	71.5(8)
O(76)-Co(3)-N(16)	95.0(8)	N(25)-Co(5)-N(26)	72.7(9)
O(4W)-Co(3)-N(16)	93.9(10)	O(6W)-Co(5)-N(26)	89.3(9)
O(76)-Co(3)-N(19)	94.9(9)	O(7W)-Co(5)-N(26)	90.2(8)
O(4W)-Co(3)-N(19)	95.1(11)	O(115)-Co(5)-N(24)	71.0(9)
N(16)-Co(3)-N(19)	69.1(9)	O(111)-Co(5)-N(24)	145.1(9)
O(76)-Co(3)-O(110)	85.4(8)	N(25)-Co(5)-N(24)	70.7(9)
O(4W)-Co(3)-O(110)	83.2(10)	O(6W)-Co(5)-N(24)	91.4(11)
N(16)-Co(3)-O(110)	148.2(9)	O(7W)-Co(5)-N(24)	89.9(9)
N(19)-Co(3)-O(110)	142.6(9)	N(26)-Co(5)-N(24)	143.4(9)

Symmetry transformations used to generate equivalent atoms: #1 -x-2,-y+4,-z+2.

8. Hydrogen bonds for compounds 1 and 2

Table S4. Hydrogen bonds for compound **1** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)
N3-H3B...O96	0.86	2.47	3.07(3)	127
N3-H3C...O2	0.86	2.48	3.07(3)	126
N14-H14A...O19W	0.86	2.17	2.97(4)	155
N14-H14B...O97	0.86	2.52	3.34(3)	159
C2-H2A...O62	0.93	2.33	3.10(3)	140
C11-H11B...O7	0.96	2.43	3.23(3)	141
C17-H17A...O82	0.93	2.48	3.20(4)	134

C22-H22B...O44	0.96	2.59	3.24(4)	126

Table S5. Hydrogen bonds for compound **2** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	∠(DHA)
N1-H1A…O93	0.86	2.46	3.03(3)	124
N1-H1B…O2	0.86	2.56	3.16(3)	127
N21-H21B…O78	0.86	2.55	3.23(4)	136
N22-H22E…O3	0.86	2.26	3.07(4)	157
N28-H28B…O19W	0.86	2.36	3.14(5)	150
C5-H5A…O85	0.93	2.17	3.00(4)	148
C11-H11C…O53	0.96	2.44	3.14(4)	130
C17-H17A…O75	0.93	2.57	3.13(4)	119
C26-H26A…O109	0.93	2.38	3.14(5)	139
C43-H43C…O64	0.96	2.41	3.34(5)	163

9. The treatment for H atoms during the refinement

Hydrogen atoms of the Schiff-base ligands were geometrically placed and refined with a riding model. The hydrogen atoms on water molecules were not included and only put into the final molecular formula.

10. The explanation of structural refinement

Since P5W30 cluster anions are very huge, LARGE Solvent Accessible VOID is found in both Structures. Which are common in the structures of polyoxometalates. Also the H atoms were not located.