<Supporting Information>

Selenotungstates incorporating organophosphonate ligands and metal ions: synthesis, characterization, magnetism and catalytic efficiency in Knoevenagel condensation reaction

Hui Kong, Peipei He, Zongfei Yang, Qiaofei Xu, Jiawei Wang, Ran Ban, Pengtao Ma, Jingping Wang* and Jingyang Niu*

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecule and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, P. R. China.

Contains

Section1: Experimental section.
Section2: The infrared spectrum of the three POTs.
Section3: The PXRD of **Co1**, **Co2** and **Ni3**.
Section4: The ball-and-stick representation of **Co1**.
Section5: The structure and the coordination mode of **Co2** and **Ni3**.
Section6: χ_M^{-1} *vs T* curve of three POTs.
Section7: The TGA curves of three POTs.
Section8: Additional catalysis related figure.
Section9: The IR spectrum and PXRD patterns after recycle catalysis.
Section10: BVS values of W, Se, Co and P atoms of compound **Co1**.
Section11: Bond length of compound **Co1**.
Section12: Angel length of compound **Co1**.
Section13: Crystallographic data of three compounds.

Experimental section

Synthesis of $Na_8H_4[Co(H_2O)_4(SeW_6O_{21})_2(CoL_2)_3]\cdot 32H_2O$ (Co1)

$Na_{24}[H_6Se_6W_{39}O_{144}]\cdot 74H_2O$ (0.60 g, 0.052 mmol) and glyphosate (0.60 g, 3.55 mmol) were dissolved in 10 mL distilled water and then $CoCl_2\cdot 6H_2O$ (0.24 g, 0.46 mmol) was added into the stirred solution until the solution dissolve completely. 15 minutes later, the 10 drops TMA were added and the pH value was carefully adjusted to about 5.9 with 6 mol/L NaOH solution. The claret-colored solution was stirred at 80 °C for 2.5 h, then the mixed solution was gradually cooled to room temperature and filtered. The colorless block shaped crystals of **Co1** were collected after about one week. Yield: 42.3% (0.159 g based on $CoCl_2\cdot 6H_2O$). Elemental analysis (%) calcd for **Co1**: H, 1.65; C, 4.01; N, 1.56; P, 3.45; Co, 4.92; Se, 2.93; W, 40.94. Found: H, 1.67; C, 4.69; N, 1.71; P, 3.52; Co, 4.89; Se, 3.26; W, 40.68. IR (KBr, cm^{-1}; s, strong; m, medium; w, weak): 3437 (s), 2112 (w), 1595 (s), 1425 (m), 1326 (s), 1303 (m), 1261 (s), 1217 (m), 1095 (s), 996 (m), 947 (s), 897 (s), 806 (s), 742 (s), 689 (s).

Synthesis of $Cs_2Na_2H_8[Co(H_2O)_4(SeW_6O_{21})_2(CoL_2)_3]\cdot 39H_2O$ (Co2)

The preparation of **Co2** was similar to **Co1**, but with 10 drops 1M CsCl instead of 10 drops TMA. The colorless block-shaped crystals of **Co2** were collected after about three days later. Yield: 36.8% (0.165 g based on $CoCl_2\cdot 6H_2O$). Elemental analysis (%) calcd for: H, 2.04; C, 3.92; N, 1.52; P, 3.37; Co, 4.27; Se, 2.86; W, 40.03. Found: H, 1.96; C, 4.23; N, 1.49; P, 3.65; Co, 4.77; Se, 3.18; W, 40.35. IR (KBr, cm^{-1}; s, strong; m, medium; w, weak): 3420 (s), 2125 (w), 1599 (s), 1423 (m), 1332 (s), 1307 (m), 1261 (w), 1222 (w), 1087 (s), 999 (s), 944 (s), 919 (s), 892 (s), 819 (s), 692 (s).

Synthesis of $Cs_2Na_2H_8[Ni(H_2O)_4(SeW_6O_{21})_2(NiL_2)_3]\cdot 36H_2O$ (Ni3)

$Na_{24}[H_6Se_6W_{39}O_{144}]\cdot 74H_2O$ (1.20 g, 0.104 mmol) and glyphosate (0.60 g, 3.55 mmol) were dissolved in 10 mL distilled water and stirred for 10 minutes. Then $NiCl_2\cdot 6H_2O$ (0.24 g, 0.46 mmol) and CsCl (0.10 g, 0.50 mmol) were added into the solution. After stirring for 30 minutes, the PH was adjusted to 5.9 with 3M NaOH aqueous. After the solution was stirred at 80 °C for 1.5h. The remaining preparation of **Ni3** was similar to **Co1**. The blue block shaped crystals of **Ni3** were collected after about ten days. Yield: 40% (0.48 g based on $NiCl_2\cdot 6H_2O$). Elemental analysis (%) calcd for: H, 1.98; C, 3.92; N, 1.52; P, 3.37; Ni, 4.26; Se, 2.87; W, 40.09; Found: H, 1.59; C, 3.79; N, 1.49; P, 3.49; Ni, 4.12; Se, 3.08; W, 39.57. IR (KBr, cm^{-1}; s, strong; m, medium; w, weak): 1602 (s), 1393 (w), 1325 (m), 1230 (m), 1081 (s), 997 (s), 937 (s), 884 (m), 785 (s), 743 (s), 694 (w), 603 (m).

The procedure of the catalysis

The ethanol (1 mL), benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol) and catalyst (0.3 mol%) were added into a tube at room temperature. Then, the mixture was stirred at the specified conditions on the parallel reactor. The product was carried on qualitative detection by GC-MS and the conversion was monitored by GC with benzaldehyde as internal standard.

As shown in **Fig. S1**, the IR spectrum showed the skeletal vibrations between 500 and 4000 cm^{-1} for three compounds, which is consistent with the result of single-crystal X-ray structural analysis. It also indicated that the polyanions in **Co1**, **Co2**, and **Ni3** are isostructural. The three compounds have obvious characteristic absorption peaks at 700−1000 cm^{-1}, which is the vibration of W−O_t and W−O−W in subunit $\{SeW_6O_{21}\}$. The absorption peaks of **Co1** at 1087 cm^{-1} and **Co2** at 1095 cm^{-1} and **Ni3** at 1097 cm^{-1} can be respectively assigned to P−O vibrations. Compared the positions of carboxyl peaks in **Co1**, **Co2** and **Ni3** with those in glyphosate, it is found that the three compounds have a certain degree of red shift in the range of 1300-1600 cm^{-1}, which may be the result of coordination between metal ions and carboxyl groups. In addition, the signal appearing at 2925 cm^{-1} (**Co1**), 2920 cm^{-1} (**Co2**) and 2912 cm^{-1} (**Ni3**) is assigned to the $\nu(CH_2)$ stretching vibration and the bands at 1583 and 1393 cm^{-1} are attributed to the carboxyl characteristic vibrations. the signals appearing around 1600cm^{-1} and the peaks around 3450cm^{-1} are belonged to the flexural vibration and stretching of lattice and coordinated water molecules.

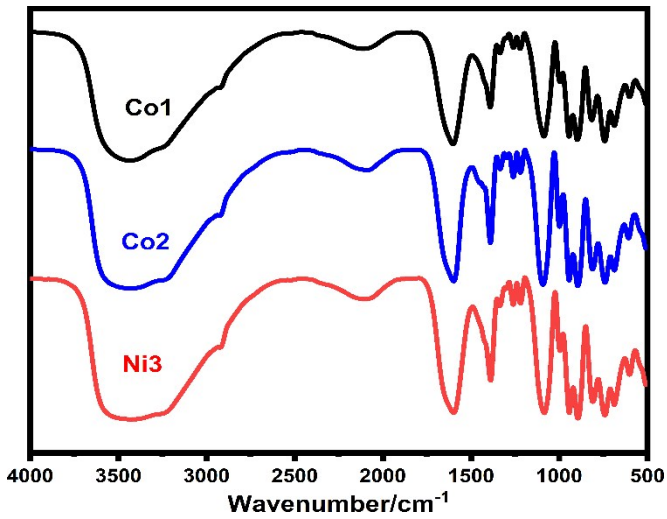

Fig.S1. The infrared spectrum of the three POMs.

As shown in **Fig. S2**, the experimental PXRD patterns for three POMs are consistent with the simulated patterns obtained from X-ray single-crystal diffraction, which indicate that the samples are pure. The differences of peak intensity between the experimental and simulated patterns might be due to the anisotropic effects of crystal.

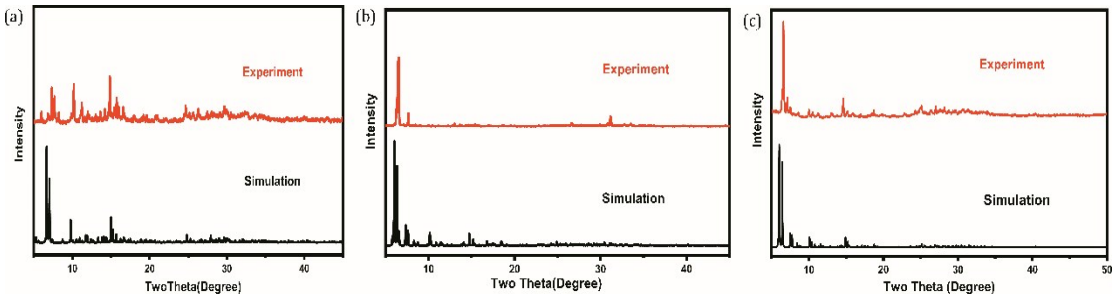

Fig.S2. The PXRD of **Co1**, **Co2** and **Ni3**.

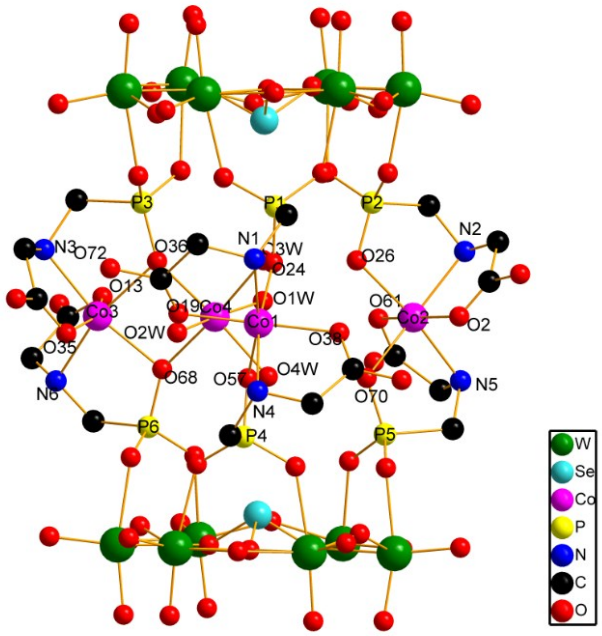

Fig. S3. The ball-and-stick representation of **Co1.**

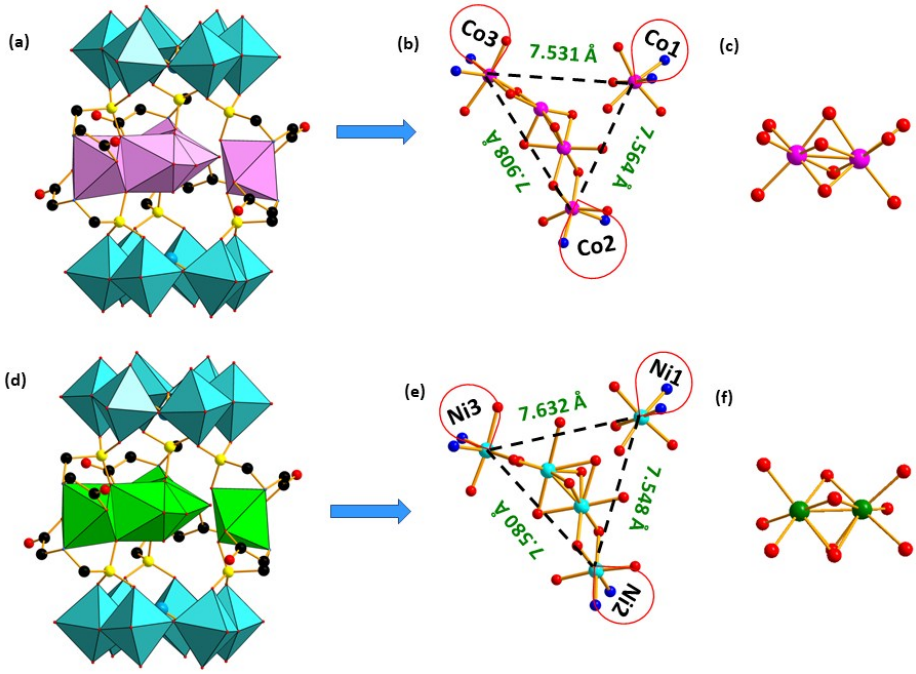

Fig. S4. (a) The polyhedral/ball-and-stick representation of **Co2**; (b) The ball-and-stick of the three Co atoms and a disordered Co atom; (d) The polyhedral/ball-and-stick representation of **Ni3**; (e) The ball-and-stick of the three Ni atoms and a disordered Ni atom, Color code: WO_6/W: blue, $\{NiO_6\}$:green, $\{CoO_6\}$: purple, P: yellow, Ni: green, C: black, N: blue, O: red. H atoms are omitted for clarity.

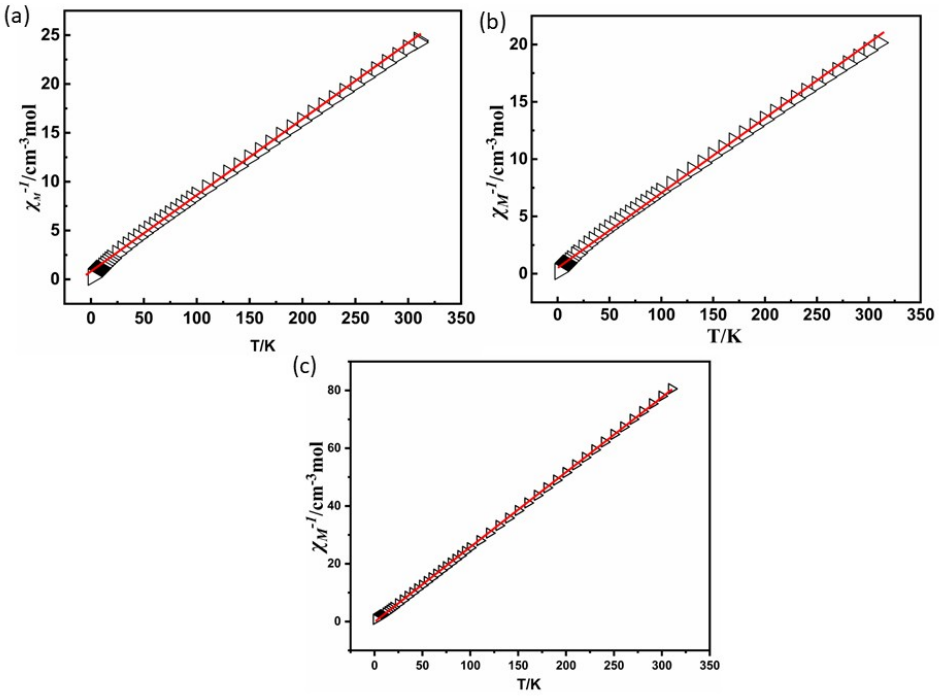

Fig. S5. χ_M^{-1} *vs T* curve of **Co1** (a), **Co2** (b), **Ni3** (c).

Under the protection of N_2, the thermogravimetric analysis (TGA) curves of **Co1**, **Co2** and **Ni3** have been measured in the range of 25–850 °C. As shown in **Fig. S6**, three compounds showed two consecutive weight loss changes. The first step is that the actual weight loss of **Co1**, is about 11.18 % (theoretical value: 11.22%), **Co2** is about 12.05 % (theoretical value: 13.12 %) and **Ni3** is about 12.05 % (theoretical value: 12.22 %) in the temperature range of 25–300 °C, which correspond to the loss of crystal water and coordination water in **Co1**, **Co2** and **Ni3**, respectively. In the second step, the mass loss is between 300–850 °C, the actual weight loss of **Co1** is about 12.13%, **Co2** is about 10.77% and **Ni3** is about 13.70%, which correspond to the loss of organic phosphonic acid fragments, structural water and the sublimation of SeO_2.

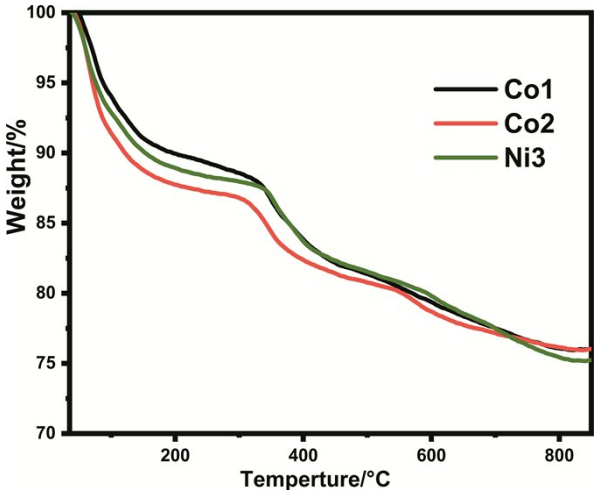

Fig. S6. The TGA curve s of three compounds.

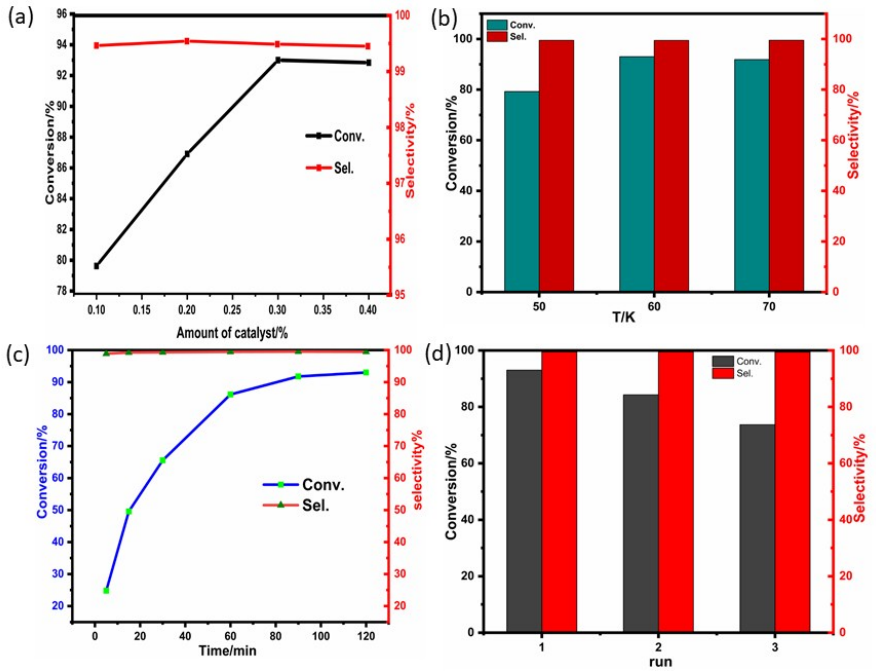

Fig. S7. (a) The influence of catalyst amount; (b) The influence of temperature; (c) Time tracking tests of **Co1**; (d) Recyclability of the **Co1** catalyst.

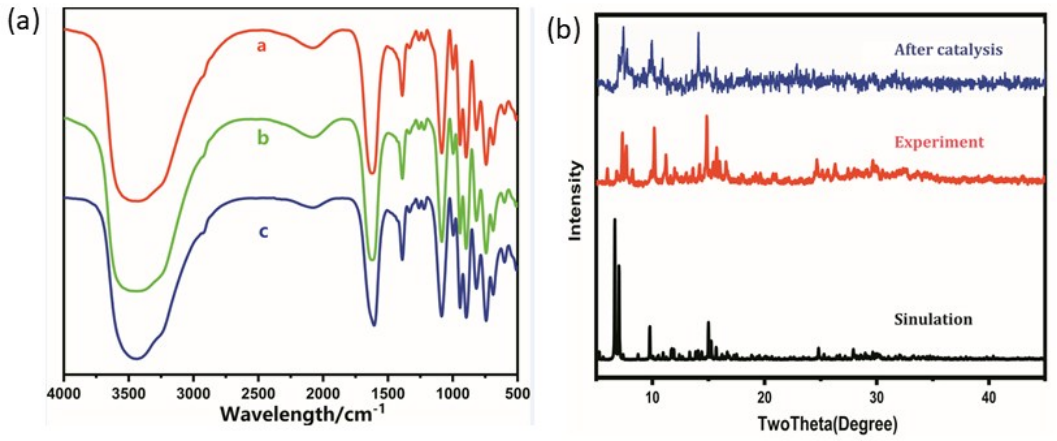

Fig. S8. (a) a: Infrared spectra of compound **Co1** before the catalytic reaction; b: After the reaction with benzaldehyde; c: After three recycled compound **Co1**. (b) PXRD patterns of **Co1** before and after recycle catalysis.

Table S1. BVS values of W, Se, Co and P atoms of compound **Co1**.

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
W1	6.11	W7	6.46	Se1	3.91	P1	4.34
W2	6.41	W8	6.36	Se2	3.77	P2	4.17
W3	6.40	W9	6.24	Co1	2.01	P3	4.28
W4	6.19	W10	6.54	Co2	2.02	P4	4.40
W5	6.37	W11	6.17	Co3	1.98	P5	4.38
W6	6.42	W12	6.38	Co4	1.96	P6	4.33

Table S2. Bond length of compound **Co1**.

Bond	Bond length	Bond	Bond length	Bond	Bond length
W1–O11	1.918(11)	W5–O4	2.281(9)	W9–O39	1.892(11)
W1–O18	1.899(10)	W5–O5	2.197(9)	W9–O42	1.930(12)
W1–O21	2.351(11)	W5–O8	1.897(12)	W9–O43	2.350(9)
W1–O22	2.144(12)	W5–O16	1.880(13)	W9–O48	2.182(9)
W1–O32	1.745(15)	W5–O29	1.741(12)	W9–O51	1.728(11)
W1–O34	1.737(15)	W5–O33	1.716(10)	W9–O66	1.753(12)
W2–O7	1.899(10)	W6–O4	2.298(11)	W10–O42	1.923(10)
W2–O10	2.155(10)	W6–O6	2.207(10)	W10–O43	2.297(11)
W2–O11	1.928(12)	W6–O8	1.944(10)	W10–O49	2.158(10)
W2–O14	1.724(11)	W6–O18	1.895(10)	W10–O53	1.900(9)
W2–O21	2.296(10)	W6–O20	1.738(12)	W10–O63	1.721(13)
W2–O28	1.732(11)	W6–O25	1.708(14)	W10–O65	1.687(16)
W3–O7	1.885(10)	W7–O45	1.902(10)	W11–O44	2.216(9)
W3–O9	2.348(11)	W7–O46	1.899(11)	W11–O50	1.916(11)
W3–O15	2.159(10)	W7–O47	2.317(11)	W11–O53	1.889(10)
W3–O23	1.917(10)	W7–O52	2.149(12)	W11–O54	2.318(11)
W3–O27	1.738(13)	W7–O64	1.743(13)	W11–O58	1.739(11)
W3–O30	1.729(13)	W7–O69	1.723(13)	W11–O62	1.716(13)
W4–O3	2.191(9)	W8–O39	1.914(11)	W12–O40	2.183(9)
W4–O9	2.309(10)	W8–O41	2.171(9)	W12–O46	1.886(11)
W4–O16	1.917(12)	W8–O45	1.953(11)	W12–O50	1.917(12)
W4–O17	1.740(12)	W8–O47	2.282(10)	W12–O54	2.302(10)
W4–O23	1.918(11)	W8–O56	1.704(11)	W12–O55	1.711(10)
W4–O31	1.748(11)	W8–O59	1.733(11)	W12–O60	1.716(10)
Se1–O4	1.713(10)	Co1–O19	2.055(13)	Co2–O2	2.052(11)
Se1–O9	1.694(10)	Co1–O24	2.098(10)	Co2–O26	2.109(10)
Se1–O21	1.704(10)	Co1–O38	2.039(14)	Co2–O61	2.057(10)
Se2–O43	1.696(10)	Co1–O57	2.140(10)	Co2–O70	2.080(9)
Se2–O47	1.709(11)	Co1–N1	2.174(13)	Co2–N2	2.156(11)
Se2–O54	1.700(9)	Co1–N4	2.156(13)	Co2–N5	2.167(13)
Co3–O35	2.028(11)	Co3–N3	2.143(13)	Co4–O3W	2.106(10)
Co3–O36	2.152(9)	Co3–N6	2.139(12)	Co4–O4W	2.083(10)
Co3–O68	2.103(10)	Co4–O1W	2.146(10)	Co4–O36	2.093(9)
Co3–O72	2.079(10)	Co4–O2W	2.109(10)	Co4–O68	2.132(9)

Table S3. Angel length of compound **Co1**.

Bond	Angel	Bond	Angel	Bond	Angel
O22–W1–O21	80.8(4)	O7–W2–O10	78.1(4)	O7–W3–O9	83.1(4)
O32–W1–O11	96.8(6)	O7–W2–O11	150.8(4)	O7–W3–O15	79.6(4)
O32–W1–O18	96.5(5)	O7–W2–O21	83.7(4)	O7–W3–O23	149.5(4)
O32–W1–O21	87.1(6)	O10–W2–O21	78.5(4)	O15–W3–O9	79.6(4)
O32–W1–O22	167.8(6)	O11–W2–O10	81.2(5)	O23–W3–O9	70.8(4)
O34–W1–O11	100.2(5)	O11–W2–O21	72.1(4)	O23–W3–O15	80.3(4)
O34–W1–O18	102.6(6)	O14–W2–O7	101.6(5)	O27–W3–O7	102.2(6)
O34–W1–O21	168.2(5)	O14–W2–O10	91.3(5)	O27–W3–O9	165.4(5)
O34–W1–O22	90.1(7)	O14–W2–O11	99.2(5)	O27–W3–O15	87.9(5)
O34–W1–O32	102.1(8)	O14–W2–O21	167.4(5)	O27–W3–O23	99.9(6)
O22–W1–O21	80.8(4)	O14–W2–O28	102.7(6)	O30–W3–O7	97.7(5)
O32–W1–O11	96.8(6)	O28–W2–O7	97.3(6)	O30–W3–O9	87.6(5)
O32–W1–O18	96.5(5)	O28–W2–O10	165.9(5)	O30–W3–O15	167.2(6)
O32–W1–O21	87.1(6)	O28–W2–O11	97.9(6)	O30–W3–O23	96.7(5)
O32–W1–O22	167.8(6)	O28–W2–O21	87.7(5)	O30–W3–O27	105.0(7)
O3–W4–O9	77.9(3)	O5–W5–O4	78.7(3)	O6–W6–O4	77.5(4)
O16–W4–O3	78.3(4)	O8–W5–O4	71.6(4)	O8–W6–O4	70.5(4)
O16–W4–O9	83.8(4)	O8–W5–O5	82.5(4)	O8–W6–O6	82.1(4)
O16–W4–O23	151.0(4)	O16–W5–O4	84.6(4)	O18–W6–O4	85.0(4)
O17–W4–O3	90.1(5)	O16–W5–O5	78.2(4)	O18–W6–O6	79.4(4)
O17–W4–O9	165.7(5)	O16–W5–O8	151.9(4)	O18–W6–O8	151.9(5)
O17–W4–O16	101.5(5)	O29–W5–O4	88.6(5)	O20–W6–O4	88.1(5)
O17–W4–O23	99.2(5)	O29–W5–O5	166.9(5)	O20–W6–O6	165.3(5)
O17–W4–O31	104.6(5)	O29–W5–O8	96.8(6)	O20–W6–O8	96.2(5)
O23–W4–O3	81.6(4)	O29–W5–O16	97.4(6)	O20–W6–O18	96.5(5)
O23–W4–O9	71.6(4)	O33–W5–O4	165.1(5)	O25–W6–O4	165.0(5)
O31–W4–O3	165.0(5)	O33–W5–O5	90.0(5)	O25–W6–O6	90.8(5)
O31–W4–O9	87.9(5)	O33–W5–O8	97.5(5)	O25–W6–O8	98.9(5)
O31–W4–O16	95.6(6)	O33–W5–O16	102.8(5)	O25–W6–O18	102.2(5)
O31–W4–O23	98.7(6)	O33–W5–O29	103.0(5)	O25–W6–O20	103.8(6)
O45–W7–O47	71.2(4)	O39–W8–O41	78.1(4)	O39–W9–O42	151.3(4)
O45–W7–O52	81.2(4)	O39–W8–O45	151.5(4)	O39–W9–O43	83.6(4)
O46–W7–O45	149.1(4)	O39–W8–O47	85.5(4)	O39–W9–O48	79.7(4)
O46–W7–O47	81.7(4)	O41–W8–O47	78.4(4)	O42–W9–Na6	125.0(3)
O46–W7–O52	79.5(4)	O45–W8–O41	81.2(4)	O42–W9–O43	71.3(4)
O52–W7–O47	79.5(4)	O45–W8–O47	71.1(4)	O42–W9–O48	82.1(4)
O64–W7–O45	101.0(5)	O56–W8–O39	101.3(5)	O48–W9–O43	79.7(3)
O64–W7–O46	103.1(5)	O56–W8–O41	92.1(5)	O51–W9–O39	101.6(5)

O64–W7–O47	167.9(6)	O56–W8–O45	98.9(5)	O51–W9–O42	100.6(5)
O64–W7–O52	90.4(6)	O56–W8–O47	167.1(5)	O51–W9–O43	167.9(5)
O69–W7–O45	95.9(5)	O56–W8–O59	102.3(6)	O51–W9–O48	90.3(5)
O69–W7–O46	98.2(6)	O59–W8–O39	96.7(5)	O51–W9–O66	103.1(6)
O69–W7–O47	88.9(6)	O59–W8–O41	165.4(5)	O66–W9–O39	95.2(5)
O69–W7–O52	168.3(6)	O59–W8–O45	98.4(6)	O66–W9–O42	97.3(5)
O69–W7–O64	101.3(8)	O59–W8–O47	87.6(5)	O66–W9–O43	87.2(5)
O42–W10–O43	72.7(4)	O44–W11–O54	80.9(4)	O40–W12–O54	78.2(4)
O42–W10–O49	82.9(4)	O50–W11–O44	80.4(4)	O46–W12–O40	78.5(4)
O49–W10–O43	77.4(4)	O50–W11–O54	70.8(4)	O46–W12–O50	150.7(4)
O53–W10–O42	151.9(4)	O53–W11–O44	78.2(4)	O46–W12–O54	83.8(4)
O53–W10–O43	83.4(4)	O53–W11–O50	148.2(4)	O50–W12–O40	81.7(4)
O53–W10–O49	77.4(4)	O53–W11–O54	82.7(4)	O50–W12–O54	71.2(4)
O63–W10–O42	97.5(5)	O58–W11–O44	167.2(5)	O55–W12–O40	90.6(4)
O63–W10–O43	87.4(6)	O58–W11–O50	97.8(5)	O55–W12–O46	102.4(5)
O63–W10–O49	163.9(7)	O58–W11–O53	97.8(4)	O55–W12–O50	99.1(5)
O63–W10–O53	96.0(5)	O58–W11–O54	86.5(5)	O55–W12–O54	166.0(5)
O65–W10–O42	99.1(6)	O62–W11–O44	90.6(5)	O55–W12–O60	102.7(5)
O65–W10–O43	167.9(5)	O62–W11–O50	100.7(6)	O60–W12–O40	166.7(5)
O65–W10–O49	93.0(6)	O62–W11–O53	102.8(6)	O60–W12–O46	97.8(5)
O65–W10–O53	101.8(6)	O62–W11–O54	168.8(5)	O60–W12–O50	96.6(5)
O65–W10–O63	102.7(7)	O62–W11–O58	102.2(6)	O60–W12–O54	88.7(5)
O9–Se1–O4	99.6(5)	O43–Se2–O47	101.1(5)	Co4–O36–Co3	97.9(4)
O9–Se1–O21	99.4(5)	O43–Se2–O54	98.1(5)	Co3–O68–Co4	98.2(4)
O21–Se1–O4	99.2(5)	O54–Se2–O47	99.4(5)		

Table S4. Crystallographic data of three compounds.

parameter	**Co1**	**Co2**	**Ni3**
Empirical formula	$C_{36}H_{48}Co_9N_{12}Na_{14}O_{202}P_{12}Se_4W_{24}$	$C_{18}H_{24}Co_4Cs_2N_6Na_2O_{87}P_6Se_2W_{12}$	$C_{18}H_{24}Cs_2N_6Na_2Ni_4O_{90}P_6Se_2W_{12}$
Formula weight	9832.97	4813.89	4861.01
T (K)	296.15	296.15	296.15
Space group	P-1	P-1	*P*-1
Crystal system	triclinic	triclinic	triclinic
a / Å	18.1321(14)	16.7391(10)	16.9074(19)
b / Å	18.8474(14)	19.6892(13)	19.793(2)
c / Å	20.3150(15)	24.9113(15)	24.551(3)
α / deg	85.5630(10)	91.1360(10)	90.418(2)
β / deg	86.4740(10)	103.4710(10)	104.442(2)
γ / deg	62.9300(10)	109.9070(10)	111.826(2)
V / Å3	6160.7(8)	7463.0(8)	7340.0(14)
Z	1	2	2
μ / mm–1	12.543	10.754	10.998
F (000)	4453.0	4312.0	4368.0
Crystal size/mm3	0.41 × 0.23 × 0.18	0.39 × 0.36 × 0.26	0.36 × 0.25 × 0.21
Limiting indices	–21 ≤ h ≤ 21	–19 ≤ h ≤ 8	-20 ≤ h ≤ 19
	–22 ≤ k ≤ 22	–20 ≤ k ≤ 23	-23 ≤ k ≤ 18
	–23 ≤ l ≤ 24	–29 ≤ l ≤ 29	-28 ≤ l ≤ 29
Reflections collected	31999	38874	38211
R_{int}	0.0448	0.0362	0.0444
GOF	1.074	1.026	0.940
R indexes [I ≥ 2σ(I)]	R1= 0.0601, wR2= 0.1596	R1= 0.0609, wR2= 0.1636	R1=0.0554, wR2= 0.1250
R indexes [all data]	R1= 0.0844, wR2= 0.1758	R1= 0.1025, wR2= 0.1923	R1=0.1081, wR2= 0.1513