Supporting information

The Highest Connected Pure Inorganic 3D Framework Assembled by $\{P_4Mo_6\}$ Cluster and Alkali Metal Potassium

He Zhang, [a,b] Kai Yu, [a,b*] Jingshen Li, [a,b] Chunmei Wang, [a,b] Jinghua Lv, [a*] Zhaoyi Chen, [a,b] Honghong Cai, [a,b] Baibin Zhou [a,b*] ,

1. Structural figures

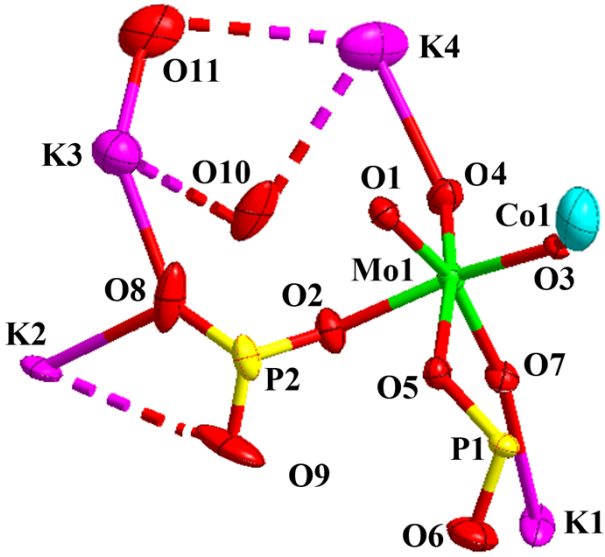

Fig. S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoids

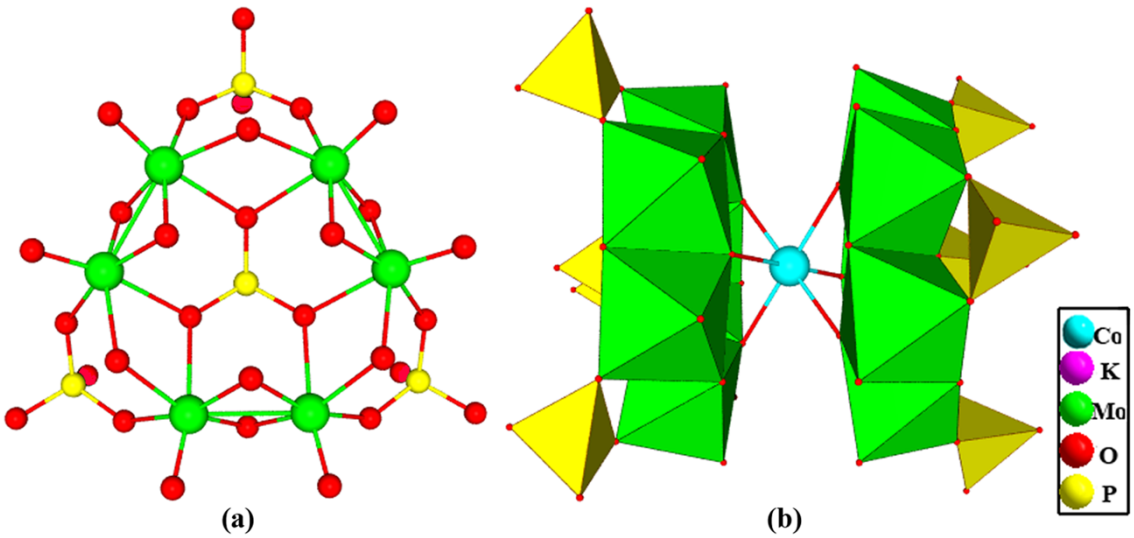

Fig. S2 (a) The basic building unit of $[P_4Mo_6O_{31}]^{12-}$ and **(b)** and its dimeric sandwich-type cluster $\{Co(P_4Mo_6X_{31})_2\}$.

* Corresponding author: Address: hlyukai188@163.com (K.Yu), zhou_bai_bin@163.com (B. B. Zhou)

2. Structural data

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

Mo(1)-O(4)	1.679(11)	Mo(1)-O(3)	1.945(13)	Mo(1)-O(1)	2.115(11)
Mo(1)-O(7)	1.930(10)	Mo(1)-O(2)	2.078(9)	Mo(1)-O(5)	2.282(8)
P(1)-O(5)	1.525(15)	P(1)-O(5)#16	1.525(15)	P(2)-O(8)	1.469(18)
P(1)-O(6)	1.50(3)	P(1)-O(5)#4	1.552(12)	P(2)-O(9)	1.488(17)
P(2)-O(2)	1.535(10)	P(2)-O(2)#17	1.535(10)		
K(1)-O(7)#3	2.719(13)	K(1)-O(7)	2.718(13)	K(1)-O(2)#3	2.712(12)
K(1)-O(2)#2	2.712(12)	K(1)-O(9)#4	2.859(12)	K(1)-O(9)#3	2.858(12)
K(2)-O(8)#5	2.561(17)	K(2)-O(8)#6	2.561(17)	K(2)-O(8)#7	2.561(17)
K(2)-O(8)#8	2.561(17)	K(2)-O(8)#9	2.561(17)	K(2)-O(8)	2.561(17)
K(3)-O(11)#5	2.47(3)	K(3)-O(11)#9	2.47(3)	K(3)-O(11)	2.47(3)
K(3)-O(8)#5	2.46(2)	K(3)-O(8)	2.46(2)	K(3)-O(8)#9	2.46(2)
K(4)-O(4)#10	2.799(11)	K(4)-O(4)#11	2.799(11)	K(4)-O(4)#12	2.799(11)
K(4)-O(4)	2.799(11)	K(4)-O(10)	3.23(3)	K(4)-O(10)#12	3.23(3)
Co(1)-O(3)#14	2.284(18)	Co(1)-O(3)#15	2.284(18)	Co(1)-O(3)#4	2.284(18)
Co(1)-O(3)	2.285(18)	Co(1)-O(3)#13	2.285(18)	Co(1)-O(3)#16	2.285(18)
O(4)-Mo(1)-O(7)	105.8(6)	O(4)-Mo(1)-O(3)	101.6(7)	O(4)-Mo(1)-O(2)	94.7(5)
O(4)-Mo(1)-O(1)	98.5(6)	O(4)-Mo(1)-O(5)	170.2(5)	O(6)-P(1)-O(5)#16	113.0(7)
O(6)-P(1)-O(5)#4	113.0(7)	O(6)-P(1)-O(5)	113.0(7)	O(6)-P(1)-O(5)#16	113.0(7)
O(8)-P(2)-O(2)#17	108.7(6)	O(8)-P(2)-O(2)	108.7(6)	O(8)-P(2)-O(9)	116.7(11)
O(3)#14-Co(1)-O(3)#15	83.3(6)	O(3)#14-Co(1)-O(3)#4	96.7(6)	O(3)#15-Co(1)-O(3)#4	83.3(6)
O(3)#14-Co(1)-O(3)	179.998(1)	O(3)#15-Co(1)-O(3)	83.6(4)	O(3)#4-Co(1)-O(3)	96.4(4)
O(3)#14-Co(1)-O(3)#13	96.4(4)	O(3)#15-Co(1)-O(3)#13	96.4(4)	O(3)#4-Co(1)-O(3)#13	83.6(4)
O(3)-Co(1)-O(3)#13	83.6(4)	O(3)#14-Co(1)-O(3)#16	83.6(4)	O(3)#15-Co(1)-O(3)#16	83.6(4)
O(3)#4-Co(1)-O(3)#16	96.4(4)	O(3)-Co(1)-O(3)#16	96.4(4)	O(3)#13-Co(1)-O(3)#16	180.0(6)
O(7)#3-K(1)-O(7)	120.4(5)	O(7)#3-K(1)-O(2)#3	61.0(2)	O(7)-K(1)-O(2)#3	176.2(4)
O(7)#3-K(1)-O(2)#2	176.2(4)	O(7)-K(1)-O(2)#2	61.0(2)	O(7)#3-K(1)-O(9)#4	125.6(5)
O(7)-K(1)-O(9)#4	102.8(5)	O(7)#3-K(1)-O(9)#3	102.9(5)	O(7)-K(1)-O(9)#3	125.5(5)
O(8)#5-K(2)-O(8)#6	107.4(10)	O(8)#5-K(2)-O(8)#7	107.4(10)	O(8)#6-K(2)-O(8)#7	72.6(10)
O(8)#5-K(2)-O(8)#8	180.0(4)	O(8)#6-K(2)-O(8)#8	72.6(10)	O(8)#7-K(2)-O(8)#8	72.6(10)
O(8)#5-K(2)-O(8)#9	72.6(10)	O(8)#6-K(2)-O(8)#9	107.4(10)	O(8)#7-K(2)-O(8)#9	179.999(4)
O(8)#8-K(2)-O(8)#9	107.4(10)	O(8)#5-K(2)-O(8)	72.6(10)	O(8)#6-K(2)-O(8)	179.999(2)
O(8)#7-K(2)-O(8)	107.4(10)	O(8)#8-K(2)-O(8)	107.4(10)	O(8)#9-K(2)-O(8)	72.6(10)
O(11)#5-K(3)-O(11)#9	79.5(9)	O(11)#5-K(3)-O(11)	79.5(9)	O(11)#9-K(3)-O(11)	79.5(9)
O(11)#5-K(3)-O(8)#5	88.6(8)	O(11)#9-K(3)-O(8)#5	137.7(3)	O(11)-K(3)-O(8)#5	138.1(3)
O(11)#5-K(3)-O(8)	137.7(3)	O(11)#9-K(3)-O(8)	138.1(3)	O(11)-K(3)-O(8)	88.6(8)
O(4)#10-K(4)-O(4)#11	76.7(4)	O(4)#10-K(4)-O(4)#12	179.999(1)	O(4)#11-K(4)-O(4)#12	103.3(4)
O(4)#10-K(4)-O(4)	103.3(4)	O(4)#11-K(4)-O(4)	179.999(1)	O(4)#12-K(4)-O(4)	76.7(4)

3. Physical characterization

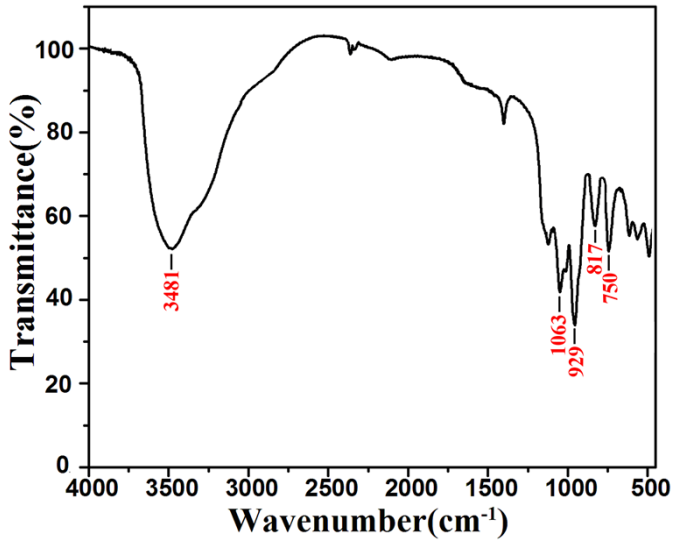

Fig. S3 IR spectra of compound **1**.

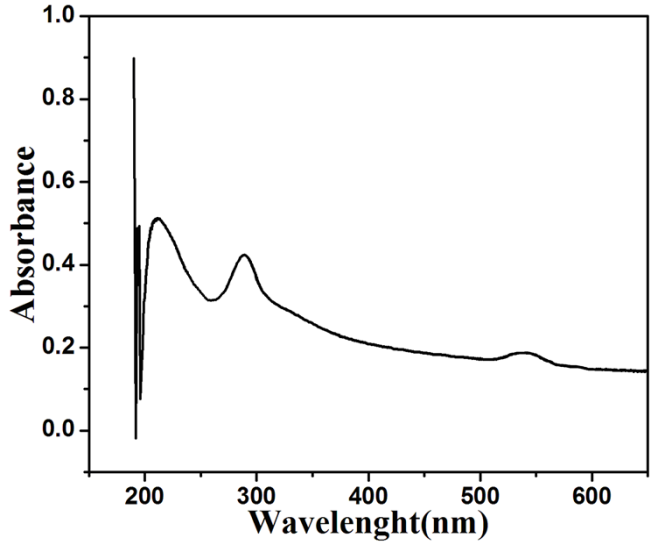

Fig. S4 Solid state UV-vis spectra of compound **1**

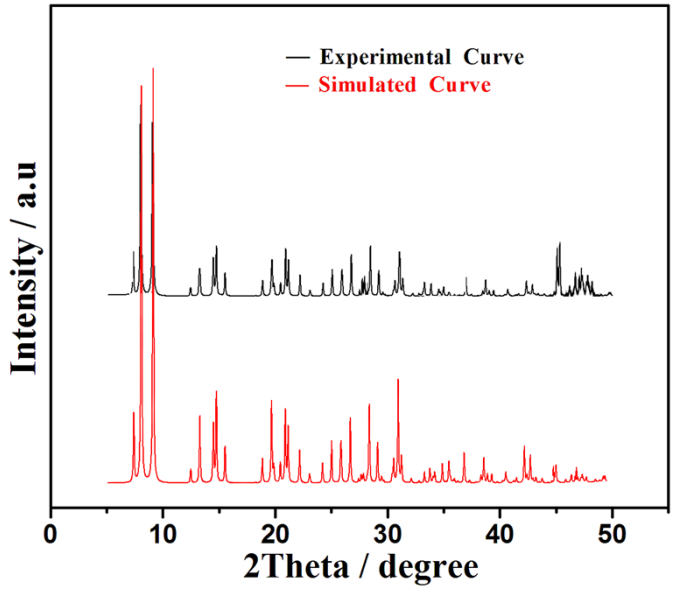

Fig. S5 The PXRD contrast curves of **1**.

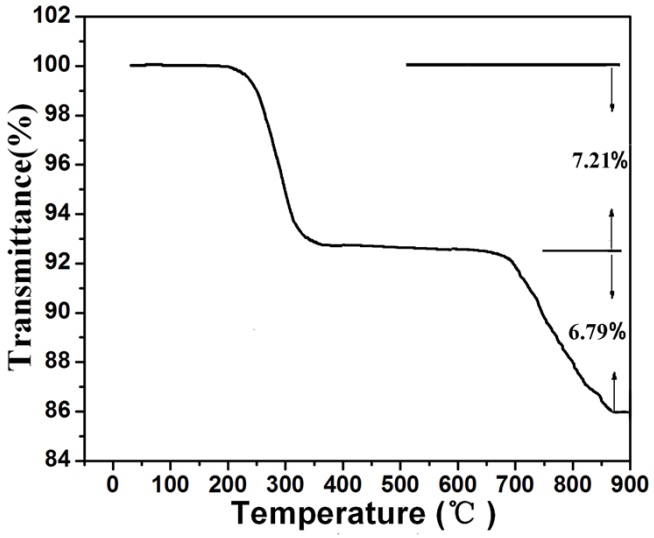

Fig. S6 TG curve of compound **1**.

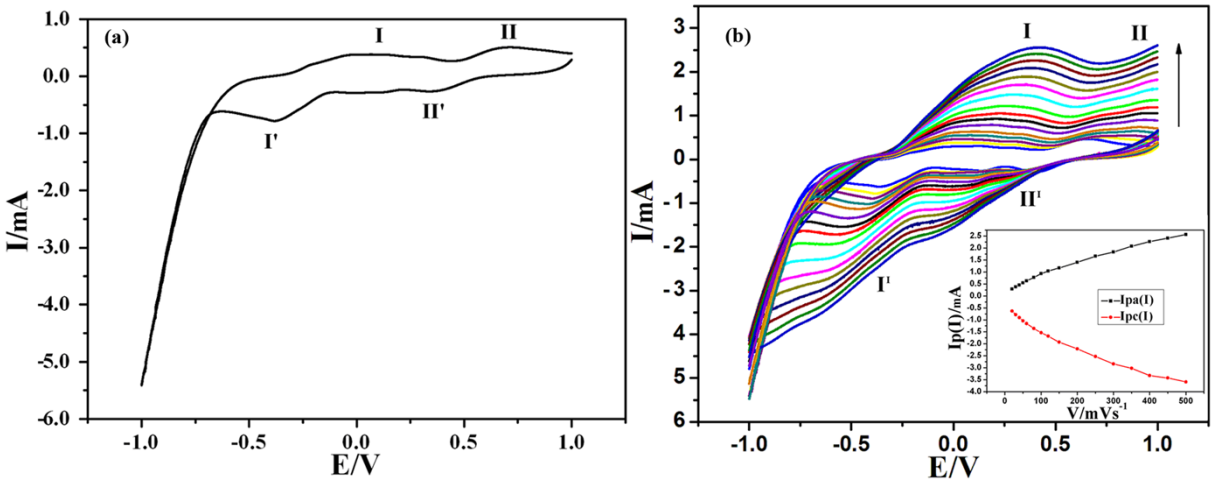

Fig. S7 (a) The CV of **1**-CPE in 1.0 M H_2SO_4 solution. Scan rate: 20 $mV \cdot s^{-1}$; (b) Cyclic voltammograms of the **1**-CPE in 1.0 M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 30, 40, 50, 60, 80, 100, 120, 150, 200, 250, 300, 350, 400, 450, 500 $mV \cdot s^{-1}$) in the potential range of +1.0 to −1.0 V. The inset shows plots of the anodic and the cathodic peak currents for II against scan rates. Potentials vs. Ag/AgCl. The arrows represent the direction of scan for anodic peak.

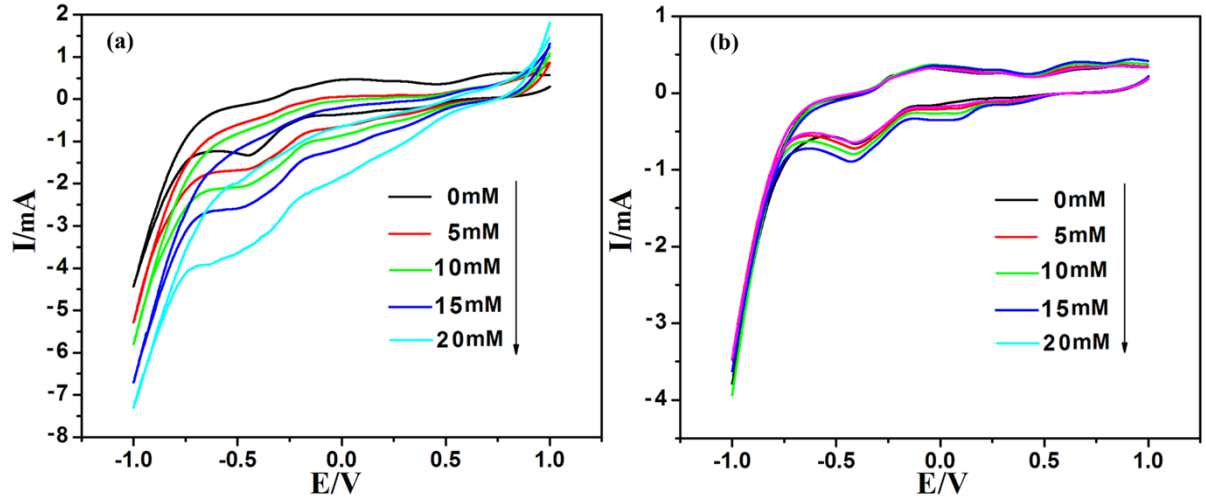

Fig. S8 Reduction of H_2O_2 (a) and ClO_3^- (b) for **1**-CPE in 1 M H_2SO_4 solution containing H_2O_2 or ClO_3^-. Scan rate: 50 $mV \cdot s^{-1}$. Potentials vs Ag/AgCl.

4. The original TOPOS result of the topological analysis

#########
1:K0.909
#########

Topology for K1
Atom K1 links by bridge ligands and has
Common vertex with R(A-A)

Co 1	0.0000	0.0000	0.0000	(0 0 0)	7.252A	1
Co 1	0.6667	0.3333	0.3333	(0 0 0)	7.252A	1

Topology for K2

Atom K2 links by bridge ligands and has
Common vertex with R(A-A)

K 3	0.3333	0.6667	0.0657	(0 0 0)	3.634A	1
K 3	0.3333	0.6667	0.2676	(0 0 0)	3.634A	1
Co 1	1.0000	1.0000	0.0000	(1 1 0)	9.758A	1
Co 1	0.0000	1.0000	0.0000	(0 1 0)	9.758A	1
Co 1	0.0000	0.0000	0.0000	(0 0 0)	9.758A	1
Co 1	0.6667	1.3333	0.3333	(0 1 0)	9.758A	1
Co 1	0.6667	0.3333	0.3333	(0 0 0)	9.758A	1
Co 1	-0.3333	0.3333	0.3333	(-1 0 0)	9.758A	1

Topology for K3

Atom K3 links by bridge ligands and has
Common vertex with R(A-A)

K 2	0.3333	0.6667	0.1667	(0 0 0)	3.634A	1
Co 1	1.0000	1.0000	0.0000	(1 1 0)	8.052A	1
Co 1	0.0000	1.0000	0.0000	(0 1 0)	8.052A	1
Co 1	0.0000	0.0000	0.0000	(0 0 0)	8.052A	1

Topology for K4

Atom K4 links by bridge ligands and has
Common vertex with R(A-A)

Co 1	1.0000	1.0000	0.0000	(1 1 0)	6.666A	1
Co 1	0.0000	0.0000	0.0000	(0 0 0)	6.666A	1

Topology for Co1

Atom Co1 links by bridge ligands and has
Common vertex with R(A-A)

K 4	0.5000	0.5000	0.0000	(0 0 0)	6.666A	1
K 4	-0.5000	-0.5000	0.0000	(-1-1 0)	6.666A	1
K 4	0.5000	0.0000	0.0000	(1 0 0)	6.666A	1
K 4	-0.5000	0.0000	0.0000	(0 0 0)	6.666A	1
K 4	0.0000	0.5000	0.0000	(0 1 0)	6.666A	1

K 4	0.0000	-0.5000	0.0000	(0 0 0)	6.666A	1
K 1	0.3333	0.0659	0.1667	(0 0 0)	7.252A	1
K 1	-0.0659	0.2674	0.1667	(0 0 0)	7.252A	1
K 1	-0.2674	-0.3333	0.1667	(0 0 0)	7.252A	1
K 1	0.2674	-0.0659	-0.1667	(0 0 0)	7.252A	1
K 1	-0.3333	-0.2674	-0.1667	(0 0 0)	7.252A	1
K 1	0.0659	0.3333	-0.1667	(0 0 0)	7.252A	1
K 1	-0.3333	-0.0659	-0.1667	(0 0 0)	7.252A	1
K 1	0.0659	-0.2674	-0.1667	(0 0 0)	7.252A	1
K 1	0.2674	0.3333	-0.1667	(0 0 0)	7.252A	1
K 1	-0.2674	0.0659	0.1667	(0 0 0)	7.252A	1
K 1	0.3333	0.2674	0.1667	(0 0 0)	7.252A	1
K 1	-0.0659	-0.3333	0.1667	(0 0 0)	7.252A	1
K 3	0.3333	0.6667	0.0657	(0 0 0)	8.052A	1
K 3	0.3333	-0.3333	0.0657	(0-1 0)	8.052A	1
K 3	-0.6667	-0.3333	0.0657	(-1-1 0)	8.052A	1
K 3	0.6667	0.3333	-0.0657	(1 1 0)	8.052A	1
K 3	-0.3333	0.3333	-0.0657	(0 1 0)	8.052A	1
K 3	-0.3333	-0.6667	-0.0657	(0 0 0)	8.052A	1
K 2	0.3333	0.6667	0.1667	(0 0 0)	9.758A	1
K 2	0.3333	-0.3333	0.1667	(0-1 0)	9.758A	1
K 2	-0.6667	-0.3333	0.1667	(-1-1 0)	9.758A	1
K 2	0.6667	0.3333	-0.1667	(1 1 0)	9.758A	1
K 2	-0.3333	0.3333	-0.1667	(0 1 0)	9.758A	1
K 2	-0.3333	-0.6667	-0.1667	(0 0 0)	9.758A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with K and Co

Coordination sequences

K1:	1	2	3	4	5	6	7	8	9	10
Num	2	55	34	450	104	1220	214	2366	364	3888
Cum	3	58	92	542	646	1866	2080	4446	4810	8698

K2:	1	2	3	4	5	6	7	8	9	10
Num	8	132	50	618	132	1480	254	2718	416	4332
Cum	9	141	191	809	941	2421	2675	5393	5809	10141

K3:	1	2	3	4	5	6	7	8	9	10
Num	4	79	91	484	246	1229	477	2314	784	3739

Cum 5 84 175 659 905 2134 2611 4925 5709 9448

K4: 1 2 3 4 5 6 7 8 9 10

Num 2 54 36 448 110 1214 224 2356 378 3874

Cum 3 57 93 541 651 1865 2089 4445 4823 8697

Co1: 1 2 3 4 5 6 7 8 9 10

Num 30 24 328 86 1002 188 2052 330 3478 512

Cum 31 55 383 469 1471 1659 3711 4041 7519 8031

TD10=8872

Vertex symbols for selected sublattice

K1 Schlafli symbol:{4}

With circuits:[4(3)]

K2 Schlafli symbol:{3^6;4^12;5^6;6^4}

With circuits:[3.3.3.3.3.3.4(3).4(3).4(3).4(3).4(3).4(3).4(4).4(4).4(4).4(4).4(4).4(4).5(6).5(6).5(6).5(6).5(6).5(6).6(18).6(48).6(48).6(48)]

K3 Schlafli symbol:{3^3;4^3}

With circuits:[3.4(4).3.4(4).3.4(4)]

K4 Schlafli symbol:{4}

With circuits:[4(4)]

CO1 Schlafli symbol:{3^6;4^84;5^36;6^213;7^27;8^69}

With circuits:[3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.5.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6.6(2).6(2).6(2).6(2).6(2).6(2).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(5).6(6).6(6).6(6).6(6).6(6).6(6).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(8).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(10).6(10).6(10).6(10).6(10).6(10).6(10).6(10).6(10).6(10).6(10).6(10).7.7.7.7.7.7.7.7.7.7.7.7.7.7.7(4).7(4).7(4).7(10).7(10).7(10).7(10).7(10).7(10).7(10).7(10).7(10).7(10).7(10).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(2).8(24).8(30).8(33).8(33).8(33).8(33).8(33).8(33)]

Total Schlafli symbol: {3^3;4^3}2{3^6;4^12;5^6;6^4}{3^6;4^84;5^36;6^213;7^27;8^69}{4}9
2,4,8,30-c net with stoichiometry (2-c)9(4-c)2(8-c)(30-c); 5-nodal net

New topology, please, contact the authors (62077 types in 9 databases)
Elapsed time: 16.18 sec.