Electronic Supplementary Material (ESI) for Dalton Transactions

A novel 2D→3D $\{Co_6PW_9\}$-based framework extended by semi-rigid bis(triazole) ligand

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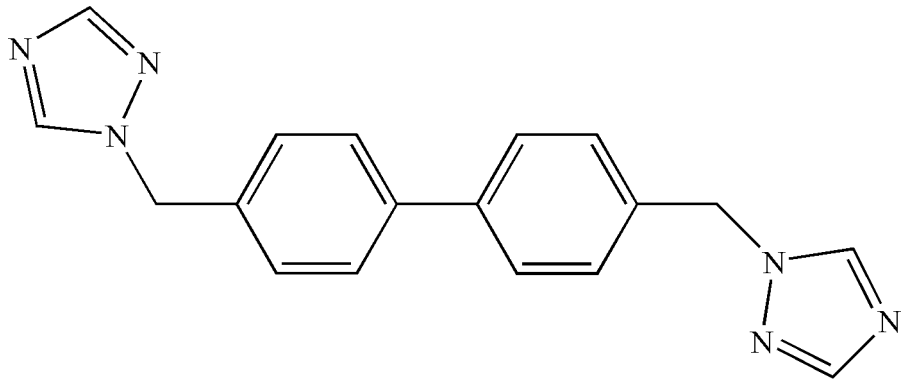

Chart. S1. The organic ligand 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (**L**) for construction of compound **1**.

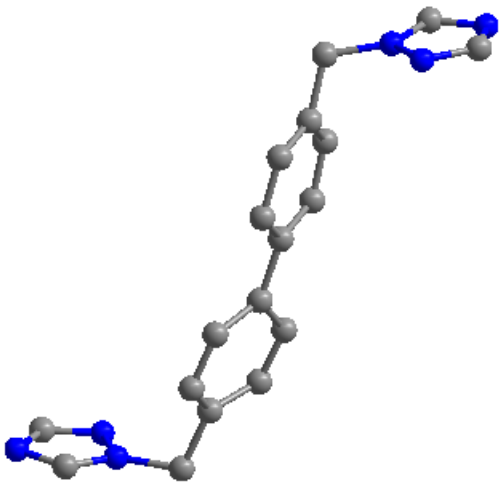

Fig. S1. The 'S'-type conformation of **L**.

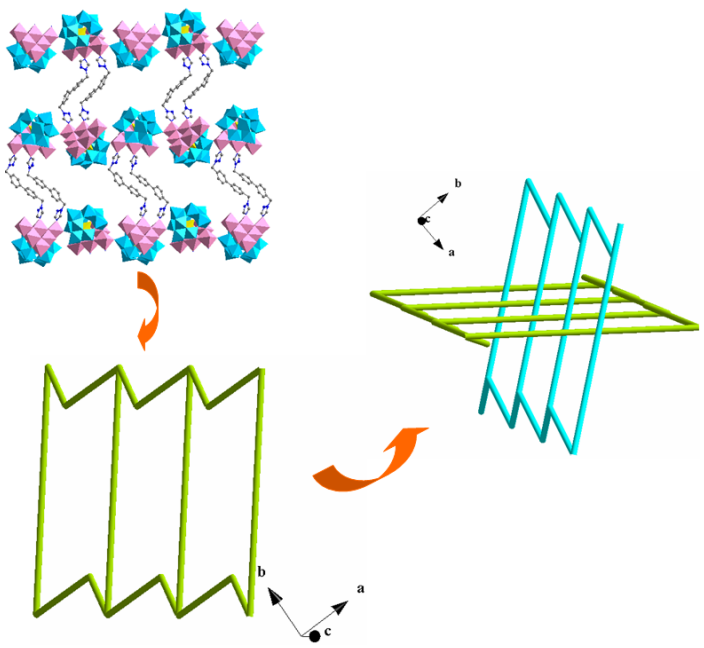

Fig. S2. The detailed interpenetration of 2D sheets in compound **1**.

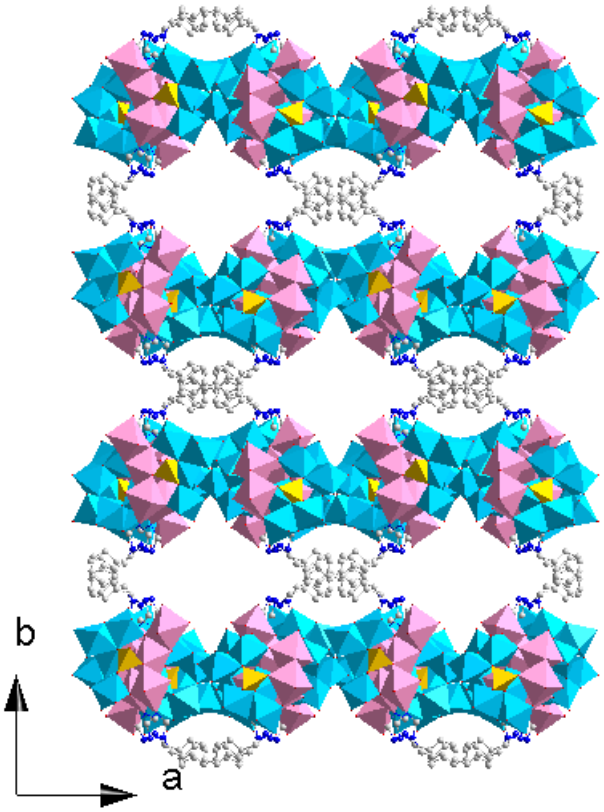

Fig. S3. The packing mode along the *c* axis in compound **1**.

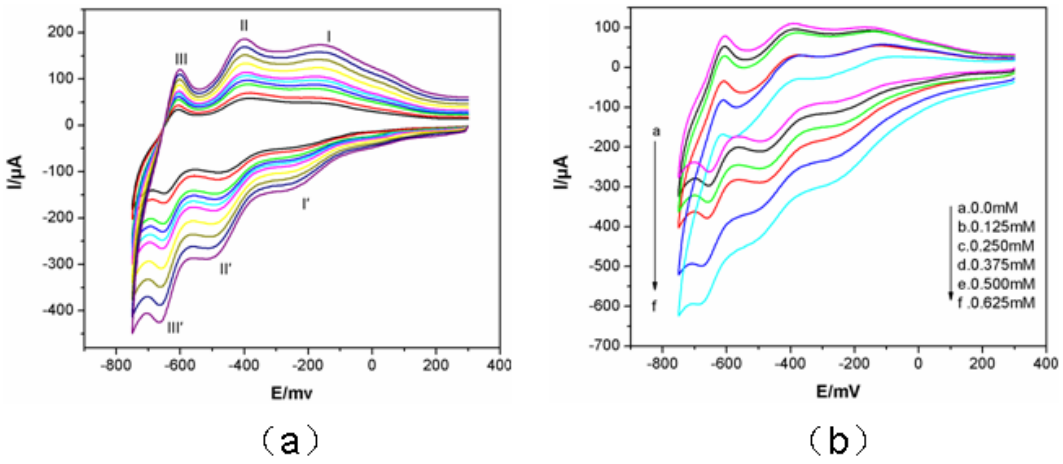

Fig. S4. (a) The cyclic voltammograms of the **1**–CPE in 1M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 60, 80, 100, 120, 140, 160, 180，200, 220 and 240 $mV{\cdot}s^{-1}$). (b) Cyclic voltammograms of the **1**–CPE in 1M H_2SO_4 aqueous solution containing 0(a); 1(b); 2(c); 3(d) ; 4(e); 5(f); 6(g) mM KNO_2. Scan rate: 200 $mV{\cdot}s^{-1}$.

Electrochemical measurements were performed with a CHI 440 Electrochemical Quartz Crystal Microbalance. A conventional three-electrode cell was used at room temperature. An SCE and a platinum wire were used as reference and auxiliary electrodes respectively. Chemically bulk-modified carbon-paste electrode (CPE) was used as the working electrode, which was prepared as the following process: 100 mg of graphite powder and 10 mg of **1**, were mixed and ground together by an agate mortar and pestle to achieve a uniform mixture, and then was added 0.1 mL of Nujol with stirring. The homogenized mixture was packed into a glass tube with a 1.5 mm inner diameter, and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

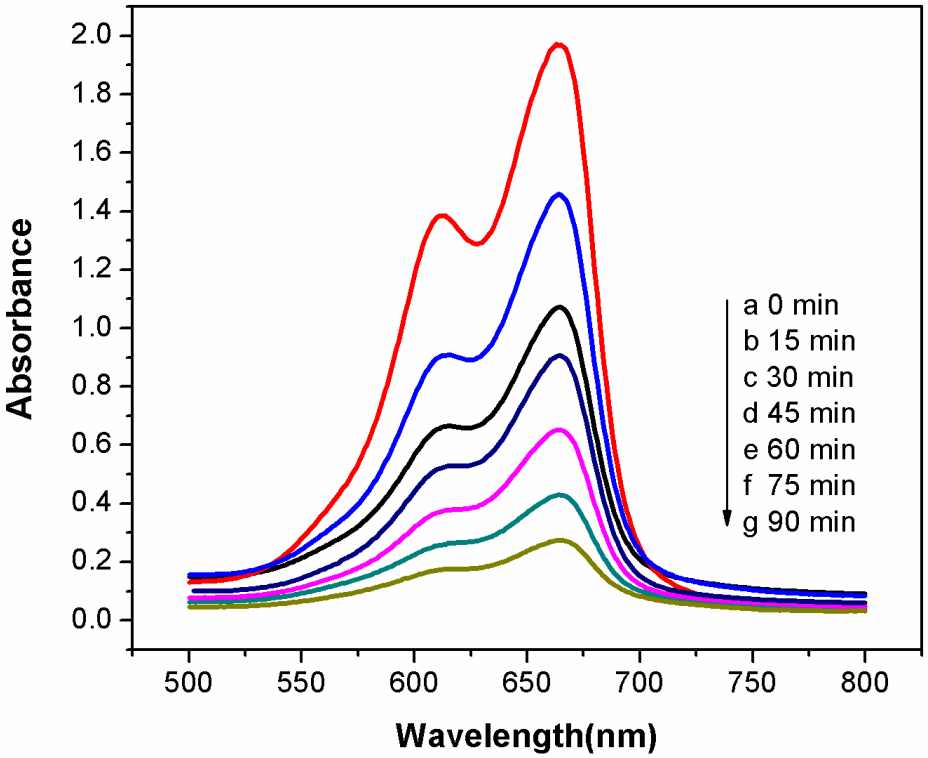

Fig. S5. Absorption spectra of the MB solution during the decomposition reaction under UV light irradiation with the use of compound **1**. Compound **1** was dispersed in the MB solution (1 mol·L^{-1}), and the suspension was magnetically stirred in the dark for 30 min to ensure the equilibrium of the working solution. Then the solution was exposed to UV irradiation from an Hg lamp, kept stirring during irradiations. A sample was taken out every 15 min for analysis.

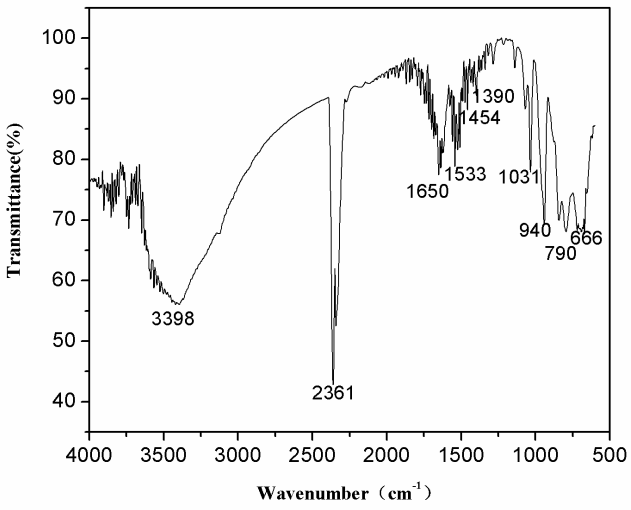

Fig. S6. IR spectrum of **1**.

In the spectrum of **1**, characteristic bands at 940, 790, and 666 cm^{-1} are attributed to the $\{PW_9\}$ anion. Bands in the regions of 1031–1650 cm^{-1} are characteristic peaks of the **L** ligand.

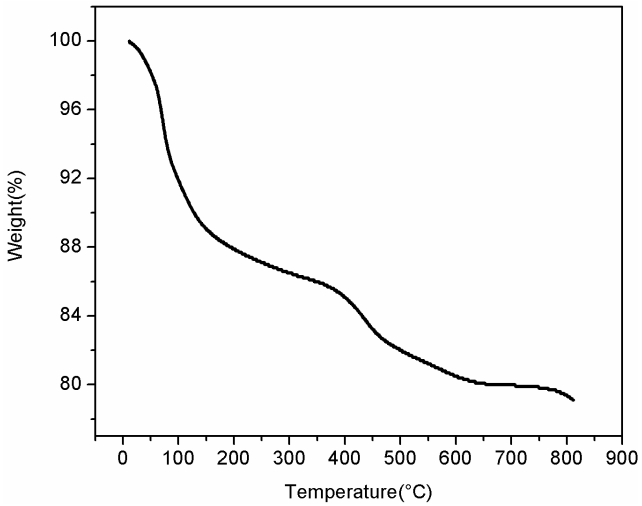

Fig. S7. The TG curve of compound **1.**

The thermogravimetric analyses (TGA) of **1** was performed under N_2 atmosphere with a heating rate of 10 °C·min^{-1} in the temperature range of 25–800 °C. The TG curve of compound **1** shows two distinct weight loss steps: The first weight loss step occurs below 160 °C corresponding to the loss of water molecules. The second weight loss step in the range of 160–800 ^{o}C can be attributed to the decomposition of **L** ligands 9.57 % (calc.10.54 %).

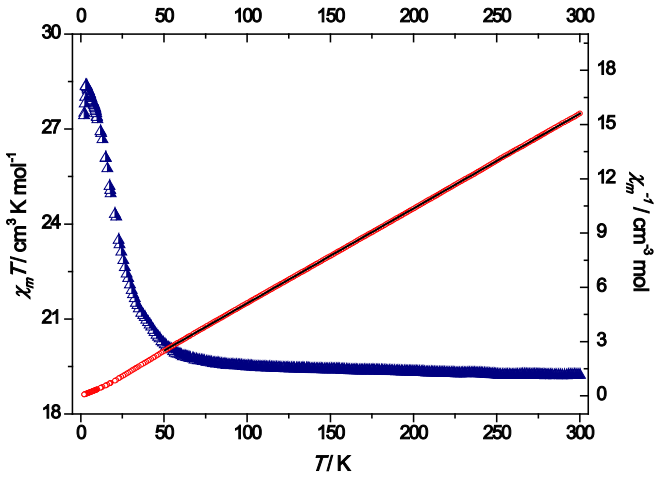

Fig. S8. The $\chi_m T$ *vs* T and χ_m^{-1} *vs* T plots in the range of 2-300 K, and the solid line is the best fit to the Curie-Weiss law.

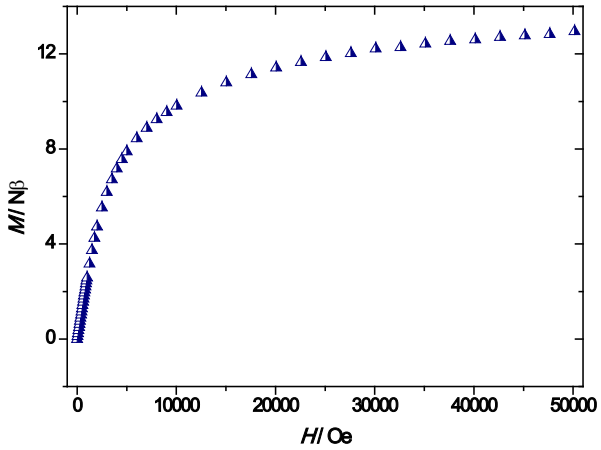

Fig. S9. The reduced magnetization at 2 K.

Table. S1. Crystal Data and Structure Refinement Parameters for Compound **1**.

formula	$C_{18}H_{16}Co_6N_6O_{46}PW_9$
fw	3091.48
cryst syst	orthorhombic
space group	P b c n
a (Å)	21.398(14)
b (Å)	32.298(14)
c (Å)	20.89(2)
V(Å^3)	14438(18)
Z	8
D_c (g cm^{-3})	2. 845
R_{int}	0.0657
GOF	1. 147
R_1[a][I>2sigma(I)]	0.0506
wR_2[b] (all data)	0. 1115

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b]$wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table. S2. Selected Bond Distances (Å) and Angles (°) for Compound **1**.

Co(1)-O(37)	2.046(11)	Co(5)-N(6)#2	2.140(15)
Co(1)-O(2W)	2.078(14)	Co(5)-O(4)	2.283(9)
Co(1)-O(1W)	2.092(13)	Co(6)-O(37)	2.050(10)
Co(1)-O(3W)	2.157(12)	Co(6)-O(26)	2.077(10)
Co(1)-O(28)	2.156(9)	Co(6)-O(28)	2.103(10)
Co(1)-O(31)	2.164(10)	Co(6)-O(35)	2.121(10)
Co(2)-O(35)	2.067(9)	Co(6)-O(9W)	2.129(11)
Co(2)-O(7W)	2.085(10)	Co(6)-O(4)	2.258(9)
Co(2)-O(4W)	2.123(10)	N(6)-Co(5)#2	2.140(15)
Co(2)-O(26)	2.127(10)	O(34)-Co(3)#3	2.125(9)
Co(2)-O(32)	2.141(10)	O(37)-Co(1)-O(2W)	176.7(5)
Co(2)-O(5W)	2.181(11)	O(37)-Co(1)-O(1W)	93.2(5)
Co(3)-O(36)	2.054(10)	O(2W)-Co(1)-O(1W)	89.3(6)
Co(3)-O(6W)	2.059(11)	O(37)-Co(1)-O(3W)	92.3(5)
Co(3)-N(1)	2.121(12)	O(2W)-Co(1)-O(3W)	89.7(5)
Co(3)-O(34)#1	2.125(9)	O(1W)-Co(1)-O(3W)	94.0(5)
Co(3)-O(19)	2.127(10)	O(37)-Co(1)-O(28)	80.9(4)
Co(3)-O(24)	2.166(9)	O(2W)-Co(1)-O(28)	96.8(5)
Co(4)-O(37)	2.053(10)	O(1W)-Co(1)-O(28)	92.0(5)
Co(4)-O(19)	2.059(10)	O(3W)-Co(1)-O(28)	171.2(5)
Co(4)-O(36)	2.096(10)	O(37)-Co(1)-O(31)	81.3(4)
Co(4)-O(31)	2.113(10)	O(2W)-Co(1)-O(31)	96.2(5)
Co(4)-O(8W)	2.130(11)	O(1W)-Co(1)-O(31)	174.0(5)
Co(4)-O(4)	2.202(9)	O(3W)-Co(1)-O(31)	88.7(4)
Co(5)-O(36)	2.065(9)	O(28)-Co(1)-O(31)	84.7(4)
Co(5)-O(35)	2.075(10)	O(35)-Co(2)-O(7W)	97.0(4)
Co(5)-O(32)	2.089(10)	O(35)-Co(2)-O(4W)	177.0(4)
Co(5)-O(24)	2.095(10)	O(7W)-Co(2)-O(4W)	85.9(4)

O(35)-Co(2)-O(26)	82.8(4)	O(19)-Co(4)-O(36)	83.0(4)
O(7W)-Co(2)-O(26)	179.2(5)	O(37)-Co(4)-O(31)	82.4(4)
O(4W)-Co(2)-O(26)	94.3(4)	O(19)-Co(4)-O(31)	97.1(4)
O(35)-Co(2)-O(32)	80.6(4)	O(36)-Co(4)-O(31)	174.2(4)
O(7W)-Co(2)-O(32)	93.0(4)	O(37)-Co(4)-O(8W)	90.9(4)
O(4W)-Co(2)-O(32)	98.5(4)	O(19)-Co(4)-O(8W)	96.1(4)
O(26)-Co(2)-O(32)	86.2(4)	O(36)-Co(4)-O(8W)	96.0(4)
O(35)-Co(2)-O(5W)	92.9(4)	O(31)-Co(4)-O(8W)	89.8(4)
O(7W)-Co(2)-O(5W)	92.0(4)	O(37)-Co(4)-O(4)	83.5(4)
O(4W)-Co(2)-O(5W)	87.8(4)	O(19)-Co(4)-O(4)	89.5(4)
O(26)-Co(2)-O(5W)	88.8(4)	O(36)-Co(4)-O(4)	84.2(4)
O(32)-Co(2)-O(5W)	172.2(4)	O(31)-Co(4)-O(4)	90.0(4)
O(36)-Co(3)-O(6W)	175.0(4)	O(8W)-Co(4)-O(4)	174.4(4)
O(36)-Co(3)-N(1)	98.0(4)	O(36)-Co(5)-O(35)	96.8(4)
O(6W)-Co(3)-N(1)	84.6(5)	O(36)-Co(5)-O(32)	169.4(4)
O(36)-Co(3)-O(34)#1	95.5(4)	O(35)-Co(5)-O(32)	81.6(4)
O(6W)-Co(3)-O(34)#1	88.8(4)	O(36)-Co(5)-O(24)	82.0(4)
N(1)-Co(3)-O(34)#1	90.3(4)	O(35)-Co(5)-O(24)	170.6(4)
O(36)-Co(3)-O(19)	82.4(4)	O(32)-Co(5)-O(24)	97.8(4)
O(6W)-Co(3)-O(19)	95.2(4)	O(36)-Co(5)-N(6)#2	101.4(5)
N(1)-Co(3)-O(19)	178.7(4)	O(35)-Co(5)-N(6)#2	100.0(5)
O(34)#1-Co(3)-O(19)	88.4(4)	O(32)-Co(5)-N(6)#2	89.1(5)
O(36)-Co(3)-O(24)	80.6(4)	O(24)-Co(5)-N(6)#2	89.4(5)
O(6W)-Co(3)-O(24)	94.9(4)	O(36)-Co(5)-O(4)	82.9(4)
N(1)-Co(3)-O(24)	95.6(4)	O(35)-Co(5)-O(4)	83.5(4)
O(34)#1-Co(3)-O(24)	173.2(4)	O(32)-Co(5)-O(4)	86.5(4)
O(19)-Co(3)-O(24)	85.6(4)	O(24)-Co(5)-O(4)	87.2(4)
O(37)-Co(4)-O(19)	173.0(4)	N(6)#2-Co(5)-O(4)	174.0(5)
O(37)-Co(4)-O(36)	96.8(4)	O(37)-Co(6)-O(26)	172.1(4)

O(37)-Co(6)-O(28)	82.1(4)	W(9)-O(24)-Co(5)	134.2(5)
O(26)-Co(6)-O(28)	98.0(4)	W(9)-O(24)-Co(3)	126.5(5)
O(37)-Co(6)-O(35)	96.0(4)	Co(5)-O(24)-Co(3)	95.9(4)
O(26)-Co(6)-O(35)	82.8(4)	W(8)-O(26)-Co(6)	132.0(5)
O(28)-Co(6)-O(35)	171.8(4)	W(8)-O(26)-Co(2)	127.2(5)
O(37)-Co(6)-O(9W)	97.8(4)	Co(6)-O(26)-Co(2)	96.5(4)
O(26)-Co(6)-O(9W)	90.0(4)	W(2)-O(28)-Co(6)	134.9(5)
O(28)-Co(6)-O(9W)	95.8(4)	W(2)-O(28)-Co(1)	126.7(5)
O(35)-Co(6)-O(9W)	92.4(4)	Co(6)-O(28)-Co(1)	95.1(4)
O(37)-Co(6)-O(4)	82.2(4)	W(4)-O(31)-Co(4)	133.8(5)
O(26)-Co(6)-O(4)	89.9(4)	W(4)-O(31)-Co(1)	127.9(5)
O(28)-Co(6)-O(4)	88.8(4)	Co(4)-O(31)-Co(1)	94.7(4)
O(35)-Co(6)-O(4)	83.1(4)	W(3)-O(32)-Co(5)	134.7(5)
O(9W)-Co(6)-O(4)	175.4(4)	W(3)-O(32)-Co(2)	125.8(5)
C(18)-N(6)-Co(5)#2	135.5(14)	Co(5)-O(32)-Co(2)	96.9(4)
C(17)-N(6)-Co(5)#2	119.2(12)	W(8)-O(34)-Co(3)#3	161.5(6)
P(1)-O(4)-Co(4)	124.1(5)	Co(2)-O(35)-Co(5)	99.7(4)
P(1)-O(4)-Co(6)	123.0(5)	Co(2)-O(35)-Co(6)	97.0(4)
Co(4)-O(4)-Co(6)	91.6(4)	Co(5)-O(35)-Co(6)	101.8(4)
P(1)-O(4)-Co(5)	125.3(5)	Co(3)-O(36)-Co(5)	100.4(4)
Co(4)-O(4)-Co(5)	91.5(3)	Co(3)-O(36)-Co(4)	97.3(4)
Co(6)-O(4)-Co(5)	91.6(3)	Co(5)-O(36)-Co(4)	101.2(4)
W(6)-O(19)-Co(4)	134.1(5)	Co(1)-O(37)-Co(6)	100.2(5)
W(6)-O(19)-Co(3)	126.1(5)	Co(1)-O(37)-Co(4)	100.3(4)
Co(4)-O(19)-Co(3)	96.2(4)	Co(6)-O(37)-Co(4)	102.5(4)

Symmetry code: #1 -x+1/2,-y+1/2,z-1/2 #2 -x,-y+1,-z+1 #3 -x+1/2,-y+1/2,z+1/2