Supporting Information

Four new metal-organic frameworks based on bi-, tetra-, penta-, and hexanuclear clusters derived from 5-(phenyldiazenyl)isophthalic acid: syntheses, structures and properties

*Hongming He,[a] Jianshi Du,[*b] Hongmin Su,[a] Yinhong Yuan,[a] Yang Song[a] and Fuxing Sun[*a]*

a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, 130012, P. R. China. Fax: +86-431-85168331; Tel: +86-431-85168887; E-mail: fxsun@jlu.edu.cn.

b China Japan Union Hospital, Jilin University, Changchun, 130031, China. E-mail: djs3043@126.com.

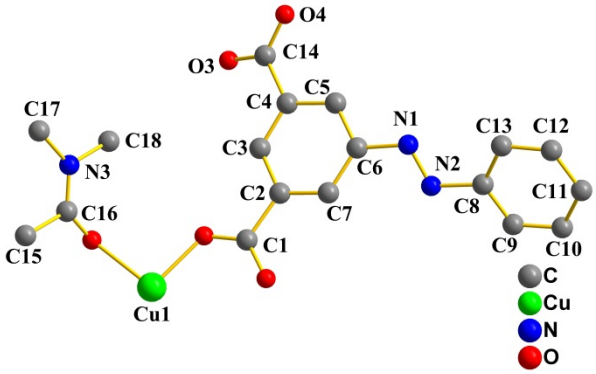


Figure S1. The asymmetric unit of **JUC-126**.

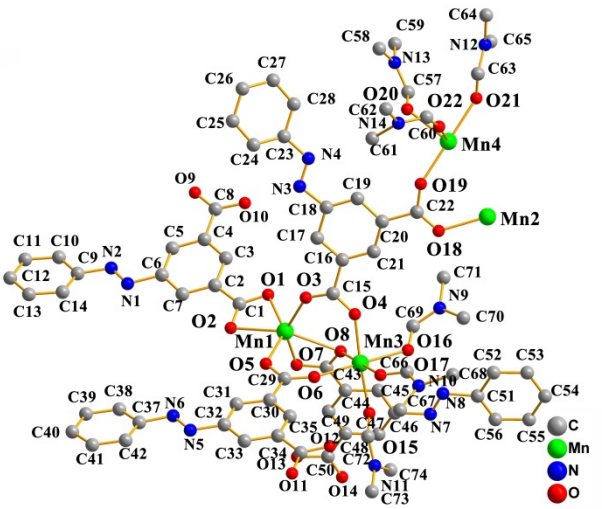


Figure S2. The asymmetric unit of **JUC-127**.

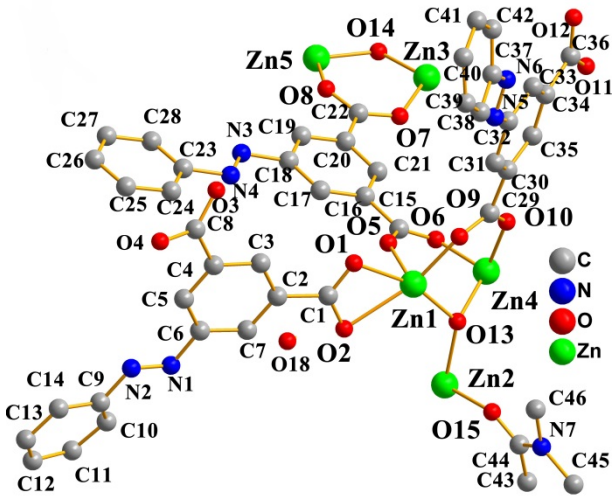


Figure S3. The asymmetric unit of **JUC-128**.

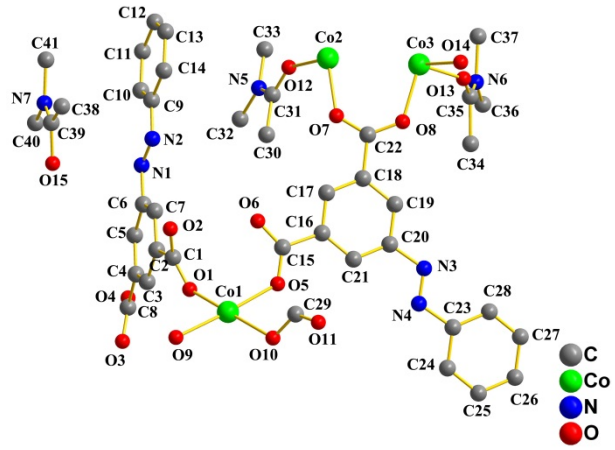


Figure S4. The asymmetric unit of **JUC-129**.

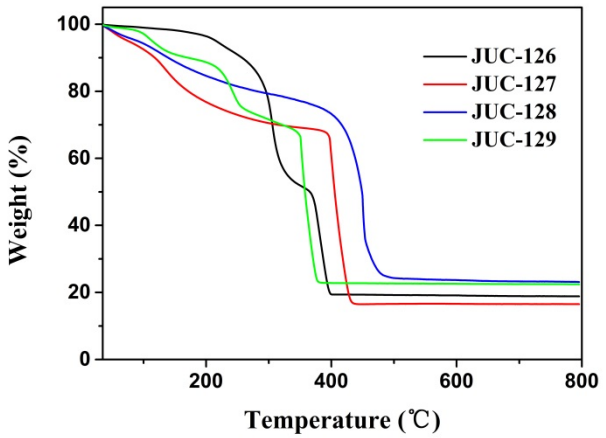


Figure S5. The TGA curves of **JUC-126**, **JUC-127**, **JUC-128** and **JUC-129**.

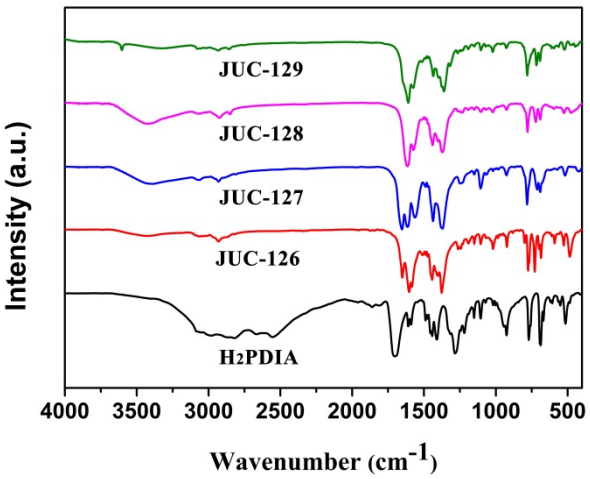
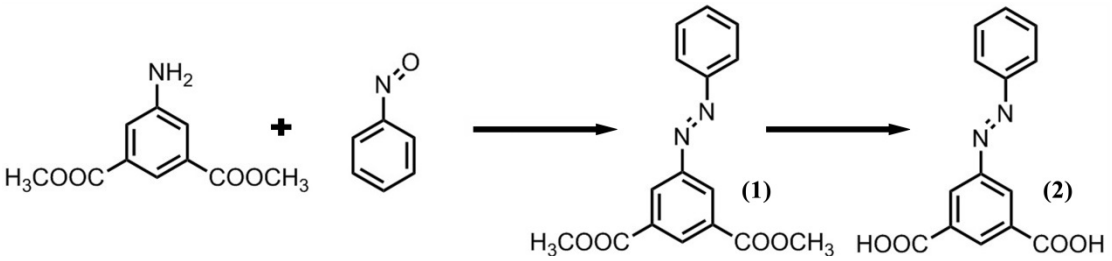


Figure S6. FT-IR spectra of **H_2PDIA**, **JUC-126**, **JUC-127**, **JUC-128** and **JUC-129**. The characteristic peak of carbonyl asymmetric stretching band (C=O) of –COOH at 1710 cm^{-1} was only found in the black curve, implying that all carboxyl groups of ligand are deprotonated.



Scheme S1. The synthetic route of **H_2PDIA**

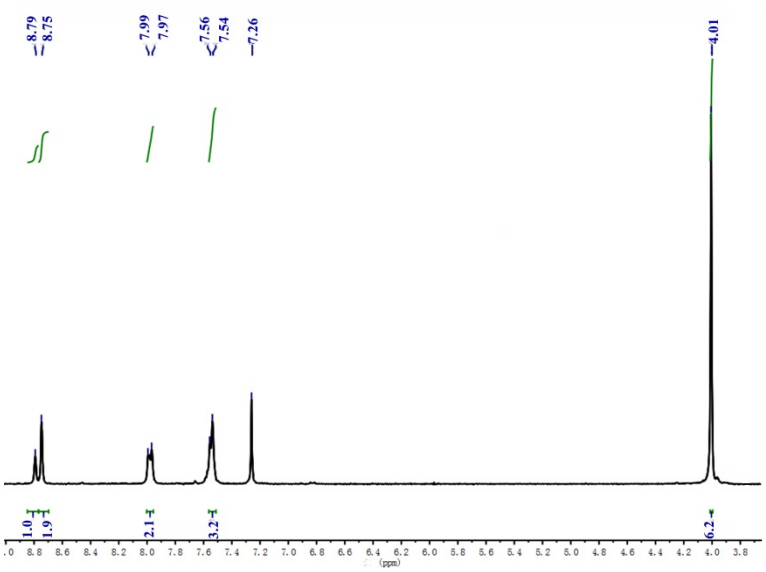


Figure S7. The ^{1}H NMR spectra of compound **1** in $CDCl_3$.

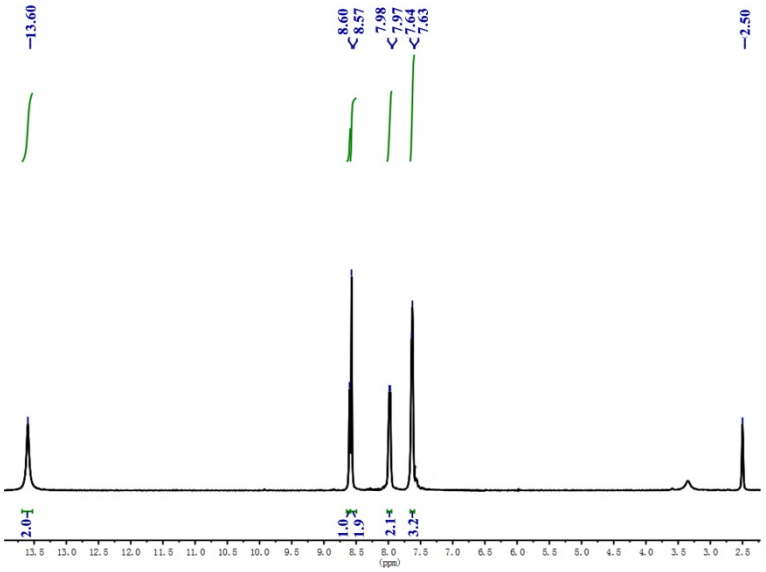


Figure S8. The ^{1}H NMR spectra of **H_2PDIA** in d_6-DMSO.

Table S1 Selected bond lengths (Å) and angles (deg) for **JUC-126, JUC-127, JUC-128** and **JUC-129**

JUC-126			
Cu(1)-O(1)	1.951(3)	Cu(1)-O(3)#1	1.966(3)
Cu(1)-O(4)#2	1.984(3)	Cu(1)-O(2)#3	1.990(3)
Cu(1)-O(5)	2.161(3)	O(4)-Cu(1)#5	1.984(3)
O(2)-Cu(1)#3	1.990(3)	O(3)-Cu(1)#4	1.966(3)
O(1)-Cu(1)-O(3)#1	88.98(15)	O(1)-Cu(1)-O(4)#2	87.94(15)
O(3)#1-Cu(1)-O(4)#2	167.64(12)	O(1)-Cu(1)-O(2)#3	167.76(12)
O(3)#1-Cu(1)-O(2)#3	89.16(14)	O(4)#2-Cu(1)-O(2)#3	91.32(14)
O(1)-Cu(1)-O(5)	94.11(14)	O(3)#1-Cu(1)-O(5)	100.81(12)
O(4)#2-Cu(1)-O(5)	91.35(12)	O(2)#3-Cu(1)-O(5)	98.13(14)

Symmetry transformations used to generate equivalent atoms:

#1 x-y, x, -z+2 #2 -x+y+1/3, -x+2/3, z-1/3 #3 -x+1/3, -y+2/3, -z+5/3 #4 y, -x+y, -z+2 #5 -y+2/3, x-y+1/3, z+1/3

JUC-127			
Mn(1)-O(3)	2.058(8)	Mn(1)-O(5)	2.061(7)
Mn(1)-O(1)	2.148(7)	Mn(1)-O(7)	2.139(7)
Mn(1)-O(2)	2.351(8)	Mn(1)-O(8)	2.478(7)

Mn(2)-O(9)#2	2.057(7)	Mn(2)-O(18)	2.095(8)
Mn(2)-O(12)#3	2.159(7)	Mn(2)-O(11)#3	2.202(7)
Mn(2)-O(13)#4	2.224(7)	Mn(2)-O(14)#4	2.310(8)
Mn(3)-O(6)	2.088(8)	Mn(3)-O(4)	2.090(6)
Mn(3)-O(16)	2.140(8)	Mn(3)-O(15)	2.151(7)
Mn(3)-O(8)	2.156(7)	Mn(3)-O(17)	2.178(8)
Mn(4)-O(19)	2.109(9)	Mn(4)-O(10)#2	2.143(8)
Mn(4)-O(21)	2.148(8)	Mn(4)-O(22)	2.152(10)
Mn(4)-O(13)#4	2.205(6)	Mn(4)-O(20)	2.223(8)
O(9)-Mn(2)#5	2.057(7)	O(10)-Mn(4)#5	2.143(8)
O(11)-Mn(2)#1	2.202(7)	O(12)-Mn(2)#1	2.159(7)
O(13)-Mn(4)#6	2.205(6)	O(13)-Mn(2)#6	2.224(7)
O(14)-Mn(2)#6	2.310(8)		
O(3)-Mn(1)-O(5)	101.1(3)	O(3)-Mn(1)-O(7)	142.2(3)
O(5)-Mn(1)-O(7)	98.5(4)	O(3)-Mn(1)-O(1)	92.8(3)
O(5)-Mn(1)-O(1)	138.3(3)	O(7)-Mn(1)-O(1)	93.6(3)
O(3)-Mn(1)-O(2)	122.7(3)	O(5)-Mn(1)-O(2)	82.6(3)
O(7)-Mn(1)-O(2)	91.6(3)	O(1)-Mn(1)-O(2)	57.1(3)
O(3)-Mn(1)-O(8)	88.2(3)	O(5)-Mn(1)-O(8)	105.8(3)
O(7)-Mn(1)-O(8)	55.3(3)	O(1)-Mn(1)-O(8)	113.8(3)
O(2)-Mn(1)-O(8)	146.3(3)	O(9)#2-Mn(2)-O(18)	89.2(3)
O(9)#2-Mn(2)-O(12)#3	157.4(3)	O(18)-Mn(2)-O(12)#3	91.0(3)
O(9)#2-Mn(2)-O(11)#3	99.8(3)	O(18)-Mn(2)-O(11)#3	102.2(3)
O(12)#3-Mn(2)-O(11)#3	58.1(3)	O(9)#2-Mn(2)-O(13)#4	100.1(3)
O(18)-Mn(2)-O(13)#4	106.6(3)	O(12)#3-Mn(2)-O(13)#4	101.5(3)
O(11)#3-Mn(2)-O(13)#4	144.9(3)	O(9)#2-Mn(2)-O(14)#4	97.3(3)
O(18)-Mn(2)-O(14)#4	163.1(3)	O(12)#3-Mn(2)-O(14)#4	88.9(3)
O(11)#3-Mn(2)-O(14)#4	92.1(3)	O(13)#4-Mn(2)-O(14)#4	56.9(3)
O(9)#2-Mn(2)-C(36)#3	128.6(3)	O(18)-Mn(2)-C(36)#3	97.8(3)

O(12)#3-Mn(2)-C(36)#3	29.2(3)	O(11)#3-Mn(2)-C(36)#3	28.9(3)
O(13)#4-Mn(2)-C(36)#3	125.6(3)	O(14)#4-Mn(2)-C(36)#3	90.4(3)
O(6)-Mn(3)-O(4)	95.1(3)	O(6)-Mn(3)-O(16)	179.0(3)
O(4)-Mn(3)-O(16)	85.7(3)	O(6)-Mn(3)-O(15)	88.7(4)
O(4)-Mn(3)-O(15)	176.2(3)	O(16)-Mn(3)-O(15)	90.4(3)
O(6)-Mn(3)-O(8)	90.3(3)	O(4)-Mn(3)-O(8)	86.6(3)
O(16)-Mn(3)-O(8)	90.1(3)	O(15)-Mn(3)-O(8)	93.8(3)
O(6)-Mn(3)-O(17)	89.9(3)	O(4)-Mn(3)-O(17)	93.0(3)
O(16)-Mn(3)-O(17)	89.7(3)	O(15)-Mn(3)-O(17)	86.6(3)
O(8)-Mn(3)-O(17)	179.6(3)	O(19)-Mn(4)-O(10)#2	90.3(3)
O(19)-Mn(4)-O(21)	178.5(4)	O(10)#2-Mn(4)-O(21)	88.2(3)
O(19)-Mn(4)-O(22)	90.2(4)	O(10)#2-Mn(4)-O(22)	174.4(3)
O(21)-Mn(4)-O(22)	91.2(3)	O(19)-Mn(4)-O(13)#4	86.8(3)
O(10)#2-Mn(4)-O(13)#4	92.9(3)	O(21)-Mn(4)-O(13)#4	93.7(3)
O(22)-Mn(4)-O(13)#4	92.7(3)	O(19)-Mn(4)-O(20)	96.9(4)
O(10)#2-Mn(4)-O(20)	88.1(3)	O(21)-Mn(4)-O(20)	82.7(3)
O(22)-Mn(4)-O(20)	86.3(4)	O(13)#4-Mn(4)-O(20)	176.2(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, y+1/2, -z #2 -x+2, y-1/2, -z+1 #3 -x+2, y-1/2, -z #4 x,y-1,z #5 -x+2, y+1/2, -z+1 #6 x, y+1, z

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O(1)-Zn(1)	2.101(3)	O(2)-Zn(1)#1	2.173(3)
O(2)-Zn(1)	2.343(4)	O(3)-Zn(5)#2	1.934(4)
O(4)-Zn(5)#3	1.903(4)	O(5)-Zn(1)	2.046(4)
O(6)-Zn(4)	1.976(4)	O(7)-Zn(3)	1.961(3)
O(8)-Zn(5)	1.972(4)	O(9)-Zn(1)	2.011(3)
O(10)-Zn(4)	1.967(3)	O(11)-Zn(4)#4	1.918(3)
O(12)-Zn(2)#4	2.067(3)	O(13)-Zn(4)	1.994(3)
O(13)-Zn(1)	2.017(3)	O(13)-Zn(2)	2.090(3)
O(14)-Zn(5)#5	1.932(2)	O(14)-Zn(5)	1.932(2)

O(14)-Zn(5)#4	1.932(2)	O(14)-Zn(3)	1.943(5)
O(15)-Zn(2)	2.115(4)	Zn(1)-O(2)#1	2.173(3)
Zn(2)-O(12)#5	2.067(3)	Zn(2)-O(12)#7	2.067(3)
Zn(2)-O(13)#1	2.090(3)	Zn(2)-O(15)#1	2.115(4)
Zn(3)-O(7)#4	1.961(3)	Zn(3)-O(7)#5	1.961(3)
Zn(4)-O(11)#5	1.918(3)	Zn(5)-O(4)#8	1.903(4)
Zn(5)-O(3)#2	1.934(4)		
O(9)-Zn(1)-O(13)	98.44(13)	O(9)-Zn(1)-O(5)	95.69(16)
O(13)-Zn(1)-O(5)	95.40(14)	O(9)-Zn(1)-O(1)	98.89(14)
O(13)-Zn(1)-O(1)	162.25(12)	O(5)-Zn(1)-O(1)	86.69(14)
O(9)-Zn(1)-O(2)#1	93.04(14)	O(13)-Zn(1)-O(2)#1	82.67(12)
O(5)-Zn(1)-O(2)#1	171.25(15)	O(1)-Zn(1)-O(2)#1	92.59(13)
O(9)-Zn(1)-O(2)	156.64(12)	O(13)-Zn(1)-O(2)	103.35(11)
O(5)-Zn(1)-O(2)	90.58(14)	O(1)-Zn(1)-O(2)	58.95(12)
O(2)#1-Zn(1)-O(2)	81.61(15)	O(12)#5-Zn(2)-O(12)#7	83.9(2)
O(12)#5-Zn(2)-O(13)#1	172.53(13)	O(12)#7-Zn(2)-O(13)#1	89.22(12)
O(12)#5-Zn(2)-O(13)	89.21(12)	O(12)#7-Zn(2)-O(13)	172.53(13)
O(13)#1-Zn(2)-O(13)	97.81(15)	O(12)#5-Zn(2)-O(15)#1	99.51(18)
O(12)#7-Zn(2)-O(15)#1	89.67(18)	O(13)#1-Zn(2)-O(15)#1	83.26(15)
O(13)-Zn(2)-O(15)#1	88.65(14)	O(12)#5-Zn(2)-O(15)	89.68(18)
O(12)#7-Zn(2)-O(15)	99.51(18)	O(13)#1-Zn(2)-O(15)	88.65(15)
O(13)-Zn(2)-O(15)	83.26(15)	O(15)#1-Zn(2)-O(15)	167.7(2)
O(14)-Zn(3)-O(7)#4	111.45(11)	O(14)-Zn(3)-O(7)#5	111.45(11)
O(7)#4-Zn(3)-O(7)#5	107.41(12)	O(14)-Zn(3)-O(7)	111.46(11)
O(7)#4-Zn(3)-O(7)	107.42(12)	O(7)#5-Zn(3)-O(7)	107.42(12)
O(11)#5-Zn(4)-O(10)	120.03(16)	O(11)#5-Zn(4)-O(6)	109.78(17)
O(10)-Zn(4)-O(6)	102.21(17)	O(11)#5-Zn(4)-O(13)	109.44(13)
O(10)-Zn(4)-O(13)	106.51(13)	O(6)-Zn(4)-O(13)	108.21(14)
O(4)#8-Zn(5)-O(14)	112.10(14)	O(4)#8-Zn(5)-O(3)#2	124.8(2)

O(14)-Zn(5)-O(3)#2	113.66(12)	O(4)#8-Zn(5)-O(8)	97.5(2)
O(14)-Zn(5)-O(8)	105.09(19)	O(3)#2-Zn(5)-O(8)	98.72(18)

Symmetry transformations used to generate equivalent atoms:

#1 x-y+1/3, -y+2/3, -z+1/6 #2 -x+2, -y+1, -z #3 x-y, x-1, -z #4 -x+y+2, -x+2, z #5 -y+2, x-y, z #6 -x+4/3, -x+y+2/3, -z+1/6 #7 -x+7/3, -x+y+2/3, -z+1/6 #8 y+1, -x+y+1, -z

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Co(1)-O(9)#1	2.048(2)	Co(1)-O(5)	2.087(3)
Co(1)-O(3)#2	2.109(3)	Co(1)-O(9)	2.128(3)
Co(1)-O(1)	2.132(3)	Co(1)-O(10)	2.273(3)
Co(2)-O(6)#3	2.017(3)	Co(2)-O(9)#4	2.034(2)
Co(2)-O(7)	2.058(2)	Co(2)-O(2)#3	2.102(2)
Co(2)-O(12)	2.126(3)	Co(2)-O(4)#5	2.143(3)
Co(3)-O(8)	2.064(3)	Co(3)-O(13)	2.075(4)
Co(3)-O(14)	2.082(3)	Co(3)-O(4)#5	2.096(2)
Co(3)-O(10)#4	2.124(3)	Co(3)-O(2)#3	2.132(3)
O(2)-Co(2)#3	2.102(2)	O(2)-Co(3)#3	2.131(3)
O(3)-Co(1)#2	2.109(3)	O(4)-Co(3)#5	2.096(2)
O(4)-Co(2)#5	2.143(3)	O(6)-Co(2)#3	2.017(3)
O(9)-Co(2)#6	2.034(2)	O(9)-Co(1)#1	2.048(2)
O(10)-Co(3)#6	2.124(3)		
O(9)#1-Co(1)-O(5)	97.37(10)	O(9)#1-Co(1)-O(3)#2	168.22(11)
O(5)-Co(1)-O(3)#2	94.15(11)	O(9)#1-Co(1)-O(9)	79.96(10)
O(5)-Co(1)-O(9)	176.86(10)	O(3)#2-Co(1)-O(9)	88.45(10)
O(9)#1-Co(1)-O(1)	93.76(10)	O(5)-Co(1)-O(1)	93.34(11)
O(3)#2-Co(1)-O(1)	83.10(10)	O(9)-Co(1)-O(1)	85.21(10)
O(9)#1-Co(1)-O(10)	91.27(10)	O(5)-Co(1)-O(10)	82.94(10)
O(3)#2-Co(1)-O(10)	92.58(10)	O(9)-Co(1)-O(10)	98.73(10)
O(1)-Co(1)-O(10)	174.10(11)	O(6)#3-Co(2)-O(9)#4	97.70(10)
O(6)#3-Co(2)-O(7)	91.88(11)	O(9)#4-Co(2)-O(7)	170.36(11)

O(6)#3-Co(2)-O(2)#3	92.48(12)	O(9)#4-Co(2)-O(2)#3	92.47(10)
O(7)-Co(2)-O(2)#3	85.99(10)	O(6)#3-Co(2)-O(12)	92.72(13)
O(9)#4-Co(2)-O(12)	80.29(10)	O(7)-Co(2)-O(12)	100.43(11)
O(2)#3-Co(2)-O(12)	171.60(11)	O(6)#3-Co(2)-O(4)#5	174.65(10)
O(9)#4-Co(2)-O(4)#5	86.75(10)	O(7)-Co(2)-O(4)#5	83.63(10)
O(2)#3-Co(2)-O(4)#5	84.33(10)	O(12)-Co(2)-O(4)#5	90.95(12)
O(8)-Co(3)-O(13)	96.82(14)	O(8)-Co(3)-O(14)	93.55(12)
O(13)-Co(3)-O(14)	89.59(15)	O(8)-Co(3)-O(4)#5	83.99(10)
O(13)-Co(3)-O(4)#5	88.79(13)	O(14)-Co(3)-O(4)#5	176.88(12)
O(8)-Co(3)-O(10)#4	169.22(11)	O(13)-Co(3)-O(10)#4	90.76(14)
O(14)-Co(3)-O(10)#4	94.16(12)	O(4)#5-Co(3)-O(10)#4	88.54(10)
O(8)-Co(3)-O(2)#3	89.56(10)	O(13)-Co(3)-O(2)#3	170.42(13)
O(14)-Co(3)-O(2)#3	97.16(12)	O(4)#5-Co(3)-O(2)#3	84.77(10)
O(10)#4-Co(3)-O(2)#3	82.01(10)		

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z+1 #2 -x+1, -y, -z+1 #3 -x, -y+1, -z+1 #4 x, y+1, z #5 -x+1, -y+1, -z+1 #6 x, y-1, z