Supporting Information

A Co_{16} cluster and a 1-D Mn chain complex supported by benzohydroxamic acid

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1. Synthesis of complex $[Co_3(bhaH)_2(phen)_2(Ac)_2(PhCO_2)_2]$ (**3**)

A mixture of $Co(O_2CMe)_2 \cdot 4H_2O$ (0.025 g, 0.1 mmol) with H_2bha (0.014 g, 0.1 mmol), 1,10-phenanthroline (0.010g, 0.05 mmol), $PhCO_2H$(0.0061 g, 0.05 mmol), methanol (1mL) was placed in a 8 mL Pyrex-tube. The tube was heated at 100 ^oC for 7 days, and then cooled to room temperature, gave orange yellow crystals of the product. The crystals were collected by filtration, washed with methanol (2 mL) and dried in air. Yield: 63%. Anal. Calc. for $C_{56}H_{42}Co_3N_6O_{12}$: C, 57.60; H, 3.63; N 7.20. Found: C,57.42; H, 3.73; N, 7.58%. Selected IR data (KBr, cm^{-1}): 3451-2670 mb, 1610s, 1516m, 1390s, 1335m, 1151s, 1024s, 903s, 840s, 724s, 703s.

2. Crystal structure of **3**

X-ray crystallographic analysis reveals that **3** crystallizes in the monoclinic *P 21/n* space group (Table S1). The three Co^{II} ions have the octahedral coordination spheres. Co1 is coordinated by two oxygen atoms from benzoic acid, two μ_2-oxygen atoms from acetic acid, and two μ_2-hydroxamate oxygen atoms from $Hhba^-$ ligand. The Co2, Co2a ions are surrounded by two nitrogen atoms from 1,10-phenanthroline, a oxygen atom from benzoic acid, a μ_2-oxygen atom from acetic acid, one carbonyl oxygen atom and a μ_2-hydroxamate oxygen atom from $Hhba^-$ ligand. The Co1-Co2 distance is 3.145 Å. Metal–ligand interatomic distances are given in Table S2.

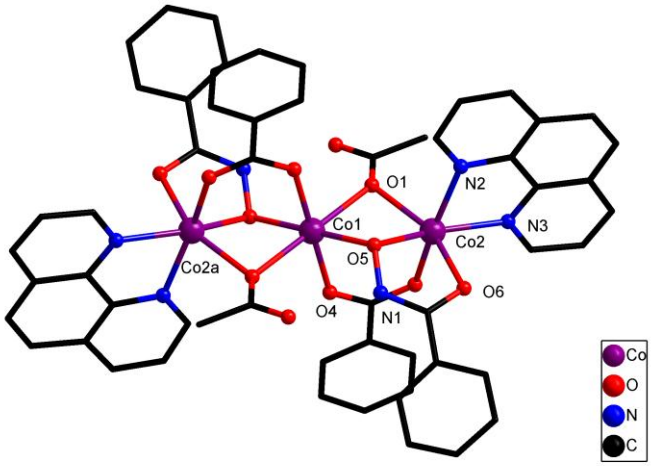

Fig. S1 Partially labeled crystal structure of **3**. Color scheme: Co^{II}, purple; O, red; N, blue. Hydrogen atoms were omitted for clarity.

3. Bond lengths and angles for complexes **1-3**

Table S1 Crystal data and structure refinement for complex **3**

complex	**3**
Empirical formula	C56H42Co3N6O12
Formula weight(g mol-1)	72.98
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 11.1144(8) Å b = 10.4303 Å c = 22.0911(17) Å α = 90° β = 96.012(2)° γ = 90°
Volume (Å3)	2546.9(3)
Z	32
ρ(Mg m-3)	1.037
F(000)	1194
Crystal size(mm)	0.32 x 0.24 x 0.19
Theta range for data collection	1.97° to 28.36°
Limiting indices	-14 ≤ h ≤ 14 -13 ≤ h ≤ 13 -28 ≤ h ≤ 29
Reflections collected / unique	17607 / 6349
Data / restraints / parameters	6349 / 0 / 350
GOF	1.067
R1, wR2[I > 2σ(I)]	R1 = 0.0411 wR2 = 0.1077
R1, wR2(all data)	R1 = 0.0689 wR2 = 0.1313
Largest diff. peak and hole(e Å-3)	0.617, -0.322

Table S2 Selected Bond Distances (Å) and Angles (°) of **3**

Co(1)-O(5)	2.0319(17)	O(4)-Co(1)-O(1)#1	89.63(7)
Co(1)-O(5)#1	2.0319(17)	O(4)#1-Co(1)-O(1)#1	90.37(7)
Co(1)-O(4)	2.0735(17)	O(1)-Co(1)-O(1)#1	180.0
Co(1)-O(4)#1	2.0735(17)	O(5)-Co(2)-O(3)	98.86(8)
Co(1)-O(1)	2.1958(17)	O(5)-Co(2)-O(6)	77.37(7)
Co(1)-O(1)#1	2.1958(17)	O(3)-Co(2)-O(6)	91.65(8)
Co(2)-O(5)	2.0313(18)	O(5)-Co(2)-N(2)	94.96(8)
Co(2)-O(3)	2.0330(19)	O(3)-Co(2)-N(2)	164.94(9)
Co(2)-O(6)	2.121(2)	O(6)-Co(2)-N(2)	97.22(8)
Co(2)-N(2)	2.121(2)	O(5)-Co(2)-N(3)	161.85(8)
Co(2)-N(3)	2.140(2)	O(3)-Co(2)-N(3)	91.54(9)
Co(2)-O(1)#1	2.1647(18)	O(6)-Co(2)-N(3)	87.55(8)
O(1)-Co(2)#1	2.1647(18)	N(2)-Co(2)-N(3)	76.77(9)
O(5)-Co(1)-O(5)#1	180.00(8)	O(5)-Co(2)-O(1)#1	78.64(7)
O(5)-Co(1)-O(4)	91.28(7)	O(3)-Co(2)-O(1)#1	86.52(7)
O(5)#1-Co(1)-O(4)	88.72(7)	O(6)-Co(2)-O(1)#1	155.36(7)
O(5)-Co(1)-O(4)#1	88.72(7)	N(2)-Co(2)-O(1)#1	90.36(8)
O(5)#1-Co(1)-O(4)#1	91.28(7)	N(3)-Co(2)-O(1)#1	117.04(8)
O(4)-Co(1)-O(4)#1	180.00(10)	Co(1)-O(5)-Co(2)	101.41(8)
O(5)-Co(1)-O(1)	102.10(7)	C(10)-O(3)-Co(2)	128.05(17)
O(5)#1-Co(1)-O(1)	77.90(7)	C(2)-O(1)-Co(2)#1	128.65(16)
O(4)-Co(1)-O(1)	90.37(7)	C(2)-O(1)-Co(1)	134.21(17)
O(4)#1-Co(1)-O(1)	89.63(7)	Co(2)#1-O(1)-Co(1)	92.29(7)
O(5)-Co(1)-O(1)#1	77.90(7)	C(3)-O(6)-Co(2)	108.38(16)
O(5)#1-Co(1)-O(1)#1	102.10(7)		

Table S3 Bond lengths [Å] and angles [deg] for complex **1**

Co(1)-O(2)	1.943(5)	Co(3)-O(11)	2.081(4)
Co(1)-O(7)	1.978(4)	Co(3)-O(4)#1	2.127(4)
Co(1)-N(2)	1.979(5)	Co(3)-O(19)	2.2776(8)
Co(1)-N(1)	1.999(5)	O(3)-Co(6)#1	2.021(4)
Co(2)-O(9)	2.044(4)	Co(4)-O(20)	2.090(5)
Co(2)-O(7)	2.066(4)	Co(4)-O(10)	2.100(5)
Co(2)-O(17)#1	2.093(4)	Co(4)-O(8)	2.104(5)
Co(2)-O(11)	2.128(4)	Co(4)-O(9)	2.131(4)
Co(2)-O(4)	2.148(4)	Co(4)-N(5)	2.131(6)
Co(2)-O(19)	2.1729(8)	Co(4)-N(4)	2.137(6)
Co(3)-O(6)#1	2.044(4)	O(4)-Co(6)#1	2.012(4)
Co(3)-O(13)	2.050(4)	O(4)-Co(3)#1	2.127(4)
Co(3)-O(15)	2.081(4)	Co(5)-O(20)	1.975(5)

Co(5)-O(12)	2.021(5)	O(17)#1-Co(2)-O(19)	85.85(11)
Co(5)-N(7)	2.092(6)	O(11)-Co(2)-O(19)	87.78(11)
Co(5)-O(11)	2.092(4)	O(4)-Co(2)-O(19)	87.83(11)
Co(5)-O(10)	2.216(5)	O(6)#1-Co(3)-O(13)	94.04(17)
O(5)-Co(8)	1.991(4)	O(6)#1-Co(3)-O(15)	167.19(15)
Co(6)-O(14)	1.935(4)	O(13)-Co(3)-O(15)	98.77(17)
Co(6)-N(8)	2.008(5)	O(6)#1-Co(3)-O(11)	89.10(15)
Co(6)-O(4)#1	2.012(4)	O(13)-Co(3)-O(11)	88.92(17)
Co(6)-O(3)#1	2.021(4)	O(15)-Co(3)-O(11)	91.09(15)
Co(6)-O(15)	2.208(4)	O(6)#1-Co(3)-O(4)#1	99.63(15)
O(6)-Co(3)#1	2.044(4)	O(13)-Co(3)-O(4)#1	99.36(17)
O(6)-Co(8)	2.092(4)	O(15)-Co(3)-O(4)#1	78.39(15)
O(6)-Co(7)	2.098(4)	O(11)-Co(3)-O(4)#1	167.44(15)
N(6)-Co(8)#1	2.015(5)	O(6)#1-Co(3)-O(19)	84.44(11)
Co(7)-O(7)	2.024(4)	O(13)-Co(3)-O(19)	174.92(14)
Co(7)-O(15)	2.034(4)	O(15)-Co(3)-O(19)	82.79(10)
Co(7)-O(17)	2.105(4)	O(11)-Co(3)-O(19)	86.21(10)
Co(7)-O(18)	2.126(4)	O(4)#1-Co(3)-O(19)	85.68(10)
Co(7)-O(19)	2.1681(7)	O(20)-Co(4)-O(10)	80.93(18)
Co(8)-O(16)	1.983(5)	O(20)-Co(4)-O(8)	168.72(18)
Co(8)-N(6)#1	2.015(5)	O(10)-Co(4)-O(8)	97.43(19)
Co(8)-O(17)	2.072(4)	O(20)-Co(4)-O(9)	92.47(17)
O(17)-Co(2)#1	2.093(4)	O(10)-Co(4)-O(9)	95.74(17)
O(19)-Co(7)#1	2.1681(7)	O(8)-Co(4)-O(9)	76.54(18)
O(19)-Co(2)#1	2.1729(8)	O(20)-Co(4)-N(5)	90.8(2)
O(19)-Co(3)#1	2.2776(8)	O(10)-Co(4)-N(5)	87.9(2)
O(2)-Co(1)-O(7)	117.3(2)	O(8)-Co(4)-N(5)	100.3(2)
O(2)-Co(1)-N(2)	111.7(2)	O(9)-Co(4)-N(5)	175.4(2)
O(7)-Co(1)-N(2)	97.73(18)	O(20)-Co(4)-N(4)	96.2(2)
O(2)-Co(1)-N(1)	118.9(2)	O(10)-Co(4)-N(4)	165.4(2)
O(7)-Co(1)-N(1)	99.32(18)	O(8)-Co(4)-N(4)	88.1(2)
N(2)-Co(1)-N(1)	109.2(2)	O(9)-Co(4)-N(4)	98.7(2)
O(9)-Co(2)-O(7)	86.49(16)	N(5)-Co(4)-N(4)	77.7(2)
O(9)-Co(2)-O(17)#1	100.99(16)	Co(6)#1-O(4)-Co(3)#1	101.16(16)
O(7)-Co(2)-O(17)#1	171.76(16)	Co(6)#1-O(4)-Co(2)	107.68(17)
O(9)-Co(2)-O(11)	87.36(16)	Co(3)#1-O(4)-Co(2)	95.38(15)
O(7)-Co(2)-O(11)	95.53(15)	O(20)-Co(5)-O(12)	159.2(2)
O(17)#1-Co(2)-O(11)	88.33(14)	O(20)-Co(5)-N(7)	102.84(19)
O(9)-Co(2)-O(4)	97.27(16)	O(12)-Co(5)-N(7)	93.4(2)
O(7)-Co(2)-O(4)	86.46(15)	O(20)-Co(5)-O(11)	97.63(17)
O(17)#1-Co(2)-O(4)	89.14(15)	O(12)-Co(5)-O(11)	92.67(18)
O(11)-Co(2)-O(4)	175.08(15)	N(7)-Co(5)-O(11)	98.60(17)
O(9)-Co(2)-O(19)	171.48(13)	O(20)-Co(5)-O(10)	80.70(18)
O(7)-Co(2)-O(19)	87.02(11)	O(12)-Co(5)-O(10)	85.05(19)

N(7)-Co(5)-O(10)	171.54(18)	O(16)-Co(8)-N(6)#1	120.0(2)
O(11)-Co(5)-O(10)	73.20(16)	O(5)-Co(8)-N(6)#1	121.8(2)
O(14)-Co(6)-N(8)	120.4(2)	O(16)-Co(8)-O(17)	77.91(17)
O(14)-Co(6)-O(4)#1	130.54(19)	O(5)-Co(8)-O(17)	141.68(18)
N(8)-Co(6)-O(4)#1	100.99(18)	N(6)#1-Co(8)-O(17)	88.47(17)
O(14)-Co(6)-O(3)#1	113.04(19)	O(16)-Co(8)-O(6)	141.01(19)
N(8)-Co(6)-O(3)#1	103.86(19)	O(5)-Co(8)-O(6)	77.99(17)
O(4)#1-Co(6)-O(3)#1	78.30(17)	N(6)#1-Co(8)-O(6)	90.25(18)
O(14)-Co(6)-O(15)	76.02(17)	O(17)-Co(8)-O(6)	79.03(15)
N(8)-Co(6)-O(15)	90.39(17)	Co(2)-O(9)-Co(4)	126.7(2)
O(4)#1-Co(6)-O(15)	77.96(15)	Co(7)-O(15)-Co(3)	99.59(16)
O(3)#1-Co(6)-O(15)	154.23(16)	Co(7)-O(15)-Co(6)	110.93(17)
Co(3)#1-O(6)-Co(8)	114.81(17)	Co(3)-O(15)-Co(6)	96.39(15)
Co(3)#1-O(6)-Co(7)	98.83(15)	Co(8)-O(17)-Co(2)#1	114.46(17)
Co(8)-O(6)-Co(7)	96.36(15)	Co(8)-O(17)-Co(7)	96.76(15)
O(7)-Co(7)-O(15)	106.21(16)	Co(2)#1-O(17)-Co(7)	96.04(15)
O(7)-Co(7)-O(6)	86.88(15)	Co(5)-O(20)-Co(4)	102.56(19)
O(15)-Co(7)-O(6)	164.76(15)	Co(7)#1-O(19)-Co(7)	180.000(1)
O(7)-Co(7)-O(17)	164.17(16)	Co(7)#1-O(19)-Co(2)	91.95(3)
O(15)-Co(7)-O(17)	88.03(15)	Co(7)-O(19)-Co(2)	88.05(3)
O(6)-Co(7)-O(17)	78.13(15)	Co(7)#1-O(19)-Co(2)#1	88.05(3)
O(7)-Co(7)-O(18)	86.55(17)	Co(7)-O(19)-Co(2)#1	91.95(3)
O(15)-Co(7)-O(18)	97.23(17)	Co(2)-O(19)-Co(2)#1	180.000(1)
O(6)-Co(7)-O(18)	91.21(16)	Co(7)#1-O(19)-Co(3)#1	89.94(3)
O(17)-Co(7)-O(18)	98.73(17)	Co(7)-O(19)-Co(3)#1	90.06(3)
O(7)-Co(7)-O(19)	88.22(11)	Co(2)-O(19)-Co(3)#1	90.49(3)
O(15)-Co(7)-O(19)	86.67(11)	Co(2)#1-O(19)-Co(3)#1	89.51(3)
O(6)-Co(7)-O(19)	85.97(10)	Co(7)#1-O(19)-Co(3)	90.06(3)
O(17)-Co(7)-O(19)	85.68(10)	Co(7)-O(19)-Co(3)	89.94(3)
O(18)-Co(7)-O(19)	174.18(13)	Co(2)-O(19)-Co(3)	89.51(3)
Co(1)-O(7)-Co(7)	112.60(19)	Co(2)#1-O(19)-Co(3)	90.49(3)
Co(1)-O(7)-Co(2)	109.73(18)	Co(3)#1-O(19)-Co(3)	180.000(1)
Co(7)-O(7)-Co(2)	95.06(15)		
O(16)-Co(8)-O(5)	102.1(2)		

Table S4 Bond lengths [Å] and angles [deg] for complex **2**

Mn(1)-O(2)#1	2.132(2)	O(1)-Mn(1)#4	2.183(3)
Mn(1)-O(2)	2.132(2)	O(2)#1-Mn(1)-O(2)	174.36(18)
Mn(1)-O(1)#2	2.183(3)	O(2)#1-Mn(1)-O(1)#2	93.04(10)
Mn(1)-O(1)#3	2.183(3)	O(2)-Mn(1)-O(1)#2	91.15(8)
Mn(1)-O(1)	2.220(3)	O(2)#1-Mn(1)-O(1)#3	91.15(8)
Mn(1)-O(1)#1	2.220(3)	O(2)-Mn(1)-O(1)#3	93.04(10)

O(1)#2-Mn(1)-O(1)#3	83.86(14)	O(2)-Mn(1)-O(1)#1	101.38(10)
O(2)#1-Mn(1)-O(1)	101.38(10)	O(1)#2-Mn(1)-O(1)#1	98.88(7)
O(2)-Mn(1)-O(1)	74.24(8)	O(1)#3-Mn(1)-O(1)#1	165.22(8)
O(1)#2-Mn(1)-O(1)	165.22(8)	O(1)-Mn(1)-O(1)#1	82.19(14)
O(1)#3-Mn(1)-O(1)	98.88(7)	Mn(1)#4-O(1)-Mn(1)	96.98(7)
O(2)#1-Mn(1)-O(1)#1	74.24(8)		

4. IR spectra for complexes **1-3**

IR spectrum of **1**

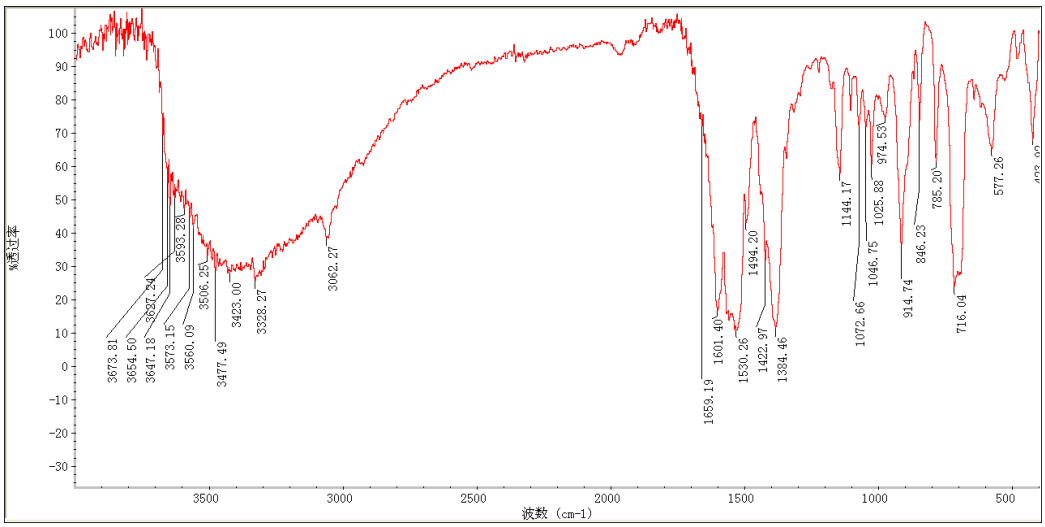

Fig. S2 The IR spectrum of complex **1**

IR spectrum of **2**

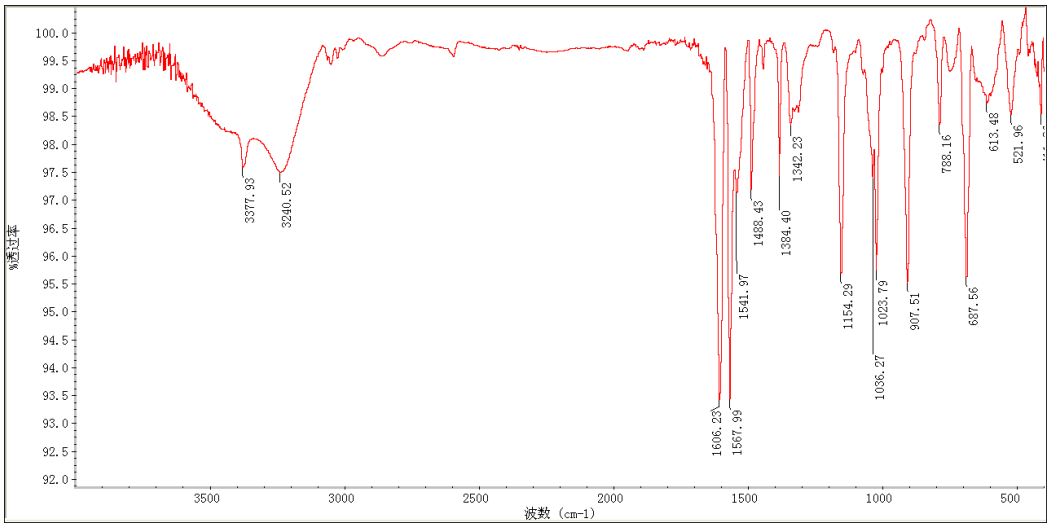

Fig. S3 The IR spectrum of complex **2**

IR spectrum of **3**

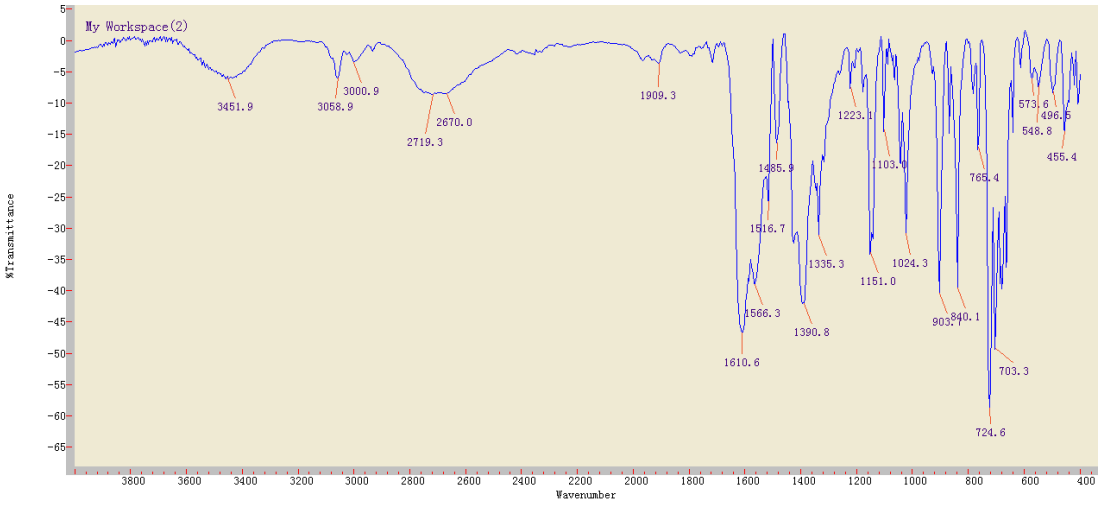

Fig. S4 The IR spectrum of complex **3**