Assembly of Various Degrees of Interpenetration Co-MOFs Based on Mononuclear or Dinuclear Cluster Units: Magnetic Properties and Gas Adsoption

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Gas Sorption Measurements: Adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area analyzer. Ultra-high-purity grade, N_2, H_2, CO_2 and CH_4 (>99.999%) were used. All of the measured sorption isotherms have been repeated twice to confirm the reproducibility. About 140 mg of samples **2** were activated at 90 °C overnight by using the "outgas" function of the surface area analyzer. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. To provide high accuracy and precision in determining P/P_0, the saturation pressure P_0 was measured throughout the N_2 analyses by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. The CO_2 isotherms were measured at 273 K and 298K, and CH_4 isotherm was measured at 273 K.

Analysis of Gas Sorption Isotherms.

The CO_2 adsorption isotherms were fitted using the Langmuir-Freundlich equation according to the literature. The Langmuir-Freundlich model gives a better fit over the entire measured pressure range and predicts the adsorption capacity of the complex **2** at saturation. The surface area of complex **2** was determined by fitting the nitrogen isotherm to the BET equation and the enthalpy of CO_2 adsorption was calculated using a modified version of the Clausius-Clapeyron equation.

$$\ln\frac{P_1}{P_2} = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \quad \text{(I)}$$

where T_1 and T_2 are the two isotherm temperatures (273 and 298 K), P_1 and P_2 are pressures at T_1 and T_2, respectively, for a given uptake, and R is the universal gas constant (R = 8.3147 J / (K· mol)). Pressure as a function of the amount of gas adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

$$\frac{q}{q_m} = \frac{b p^{(1/t)}}{1 + b p^{(1/t)}} \qquad (\text{II}) \qquad \text{where } q = \text{the amount adsorbed}$$

q_m = the amount adsorbed at saturation

p = pressure

b and t = constants.

Equation (**II**) rearranges to:

$$p = \left(\frac{q / q_m}{b - bq / q_m}\right)^t \qquad (\text{III})$$

$$\Delta H_{ads} = \frac{RT_1T_2}{T_2 - T_1} \times \ln \frac{\left(\frac{q / q_{m1}}{b_1 - b_1 q / q_{m1}}\right)^{t1}}{\left(\frac{q / q_{m2}}{b_2 - b_2 q / q_{m2}}\right)^{t2}} \qquad (\text{IV})$$

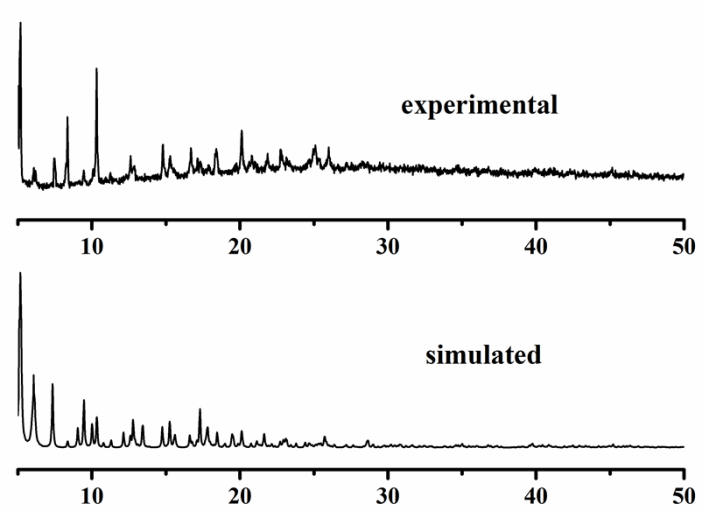

Fig. S1 PXRD spectra of complex **2**

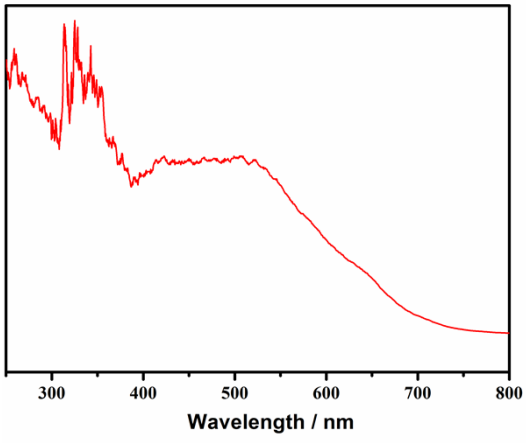

Fig. S2 UV-vis absorbance spectra of complex **2** at room temperature

For compound **1**: "The PLATON SQUEEZE procedure was used to treat regions of diffuse solvent which could not be sensibly modelled in terms of atomic sites. Their contribution to the diffraction pattern was removed and modified F_o^2 written to a new HKL file. The number of electrons thus located, 105 per unit cell. This residual electron density was assigned to two molecules of the water, [105/4 = 21e per a ligand; two molecules of the water would give 20e]."

For compound **2**: "The PLATON SQUEEZE procedure was used to treat regions of diffuse solvent which could not be sensibly modelled in terms of atomic sites. Their contribution to the diffraction pattern was removed and modified F_o^2 written to a new HKL file. The number of electrons thus located, 380 per unit cell. This residual electron density was assigned to two molecules of DMA, [380/4 = 95e per a ligand; two molecules of the DMA would give 96e]."

For compound **3**: "The PLATON SQUEEZE procedure was used to treat regions of diffuse solvent which could not be sensibly modelled in terms of atomic sites. Their contribution to the diffraction pattern was removed and modified F_o^2 written to a new HKL file. The number of electrons thus located, 276 per unit cell. This residual electron density was assigned to three and a half molecules of water, [276/8 = 34e per half of a ligand; three and a half molecules of water would give 34e]."

Table S1. Bond lengths [Å] and angles [deg] for complex **1**.

Co(1)-O(1)	2.0211(16)
Co(1)-O(4)	2.0253(16)
Co(1)-N(4)#2	2.1887(12)
Co(1)-N(4)#3	2.1887(12)
Co(1)-N(1)	2.1932(13)
Co(1)-N(1)#4	2.1932(13)
O(1)-Co(1)-O(4)	177.79(6)
O(1)-Co(1)-N(4)#2	95.22(5)
O(4)-Co(1)-N(4)#2	86.40(5)
O(1)-Co(1)-N(4)#3	95.22(5)
O(4)-Co(1)-N(4)#3	86.40(5)
N(4)#2-Co(1)-N(4)#3	85.46(6)
O(1)-Co(1)-N(1)	90.20(5)
O(4)-Co(1)-N(1)	88.26(5)
N(4)#2-Co(1)-N(1)	91.06(5)
N(4)#3-Co(1)-N(1)	173.80(5)
O(1)-Co(1)-N(1)#4	90.20(5)
O(4)-Co(1)-N(1)#4	88.26(5)
N(4)#2-Co(1)-N(1)#4	173.80(5)
N(4)#3-Co(1)-N(1)#4	91.06(5)
N(1)-Co(1)-N(1)#4	91.93(8)

Symmetry transformations used to generate equivalent atoms:

#1: *x*, -*y*+1/2, -*z*+2 #2: *x*+1, *y*+1, *z*

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

#5: *x*-1, *y*-1, *z*

Table S2. Bond lengths [Å] and angles [deg] for complex **2**.

Co(1)-O(2)	2.0508(10)
Co(1)-O(1)#3	2.0720(9)
Co(1)-O(4)#4	2.0990(10)
Co(1)-N(1)	2.1441(11)
Co(1)-N(3')#5	2.152(5)
Co(1)-O(5)	2.1629(6)
Co(1)-N(3)#5	2.1975(15)
O(1)-Co(1)#3	2.0720(9)
O(4)-Co(1)#6	2.0990(10)

O(5)-Co(1)#3	2.1629(6)
O(2)-Co(1)-O(1)#3	95.11(4)
O(2)-Co(1)-O(4)#4	176.67(4)
O(1)#3-Co(1)-O(4)#4	88.21(4)
O(2)-Co(1)-N(1)	91.87(4)
O(1)#3-Co(1)-N(1)	89.36(4)
O(4)#4-Co(1)-N(1)	88.13(4)
O(2)-Co(1)-N(3')#5	87.13(15)
O(1)#3-Co(1)-N(3')#5	176.39(14)
O(4)#4-Co(1)-N(3')#5	89.55(15)
N(1)-Co(1)-N(3')#5	93.40(13)
O(2)-Co(1)-O(5)	91.75(3)
O(1)#3-Co(1)-O(5)	87.61(3)
O(4)#4-Co(1)-O(5)	88.41(3)
N(1)-Co(1)-O(5)	175.47(3)
N(3')#5-Co(1)-O(5)	89.50(13)
O(2)-Co(1)-N(3)#5	87.35(5)
O(1)#3-Co(1)-N(3)#5	175.34(5)
O(4)#4-Co(1)-N(3)#5	89.33(5)
N(1)-Co(1)-N(3)#5	94.53(5)
O(5)-Co(1)-N(3)#5	88.36(5)

Symmetry transformations used to generate equivalent atoms:

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

Table S3 Bond lengths [Å] and angles [deg] for complex **3**.

Co(1)-O(1)	1.9825(18)
Co(1)-O(2)#3	2.1043(18)
Co(1)-N(4)#4	2.113(2)
Co(1)-O(1W)	2.1481(17)
Co(1)-O(3)#5	2.1799(18)
O(3)-Co(1)#7	2.1800(18)
O(1)-Co(1)-O(2)#3	100.57(7)
O(1)-Co(1)-N(4)#4	94.62(8)
O(2)#3-Co(1)-N(4)#4	87.65(7)
O(1)-Co(1)-O(1W)	80.68(7)

O(2)#3-Co(1)-O(1W)	177.29(7)
N(4)#4-Co(1)-O(1W)	89.86(8)
O(1)-Co(1)-O(3)#5	163.82(7)
O(2)#3-Co(1)-O(3)#5	94.44(7)
N(4)#4-Co(1)-O(3)#5	91.97(8)
O(1W)-Co(1)-O(3)#5	84.58(7)
O(1)-Co(1)-N(3)	86.30(8)
O(2)#3-Co(1)-N(3)	88.79(7)
N(4)#4-Co(1)-N(3)	176.43(8)
O(1W)-Co(1)-N(3)	93.70(7)
O(3)#5-Co(1)-N(3)	88.04(7)

Symmetry transformations used to generate equivalent atoms:

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