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Various metal-pyrazole loops tuned polyoxometalate-based Cu^{II}/Co^{II} complexes: Design, diverse architectures and catalytic activity toward the oxidation of thioether derivatives

Jing-Yuan Zhang [a, b] ‡, Yu-Chen Zhang [a] ‡, Xiu-Li Wang [a*], Zhi-Han Chang [a], Zhong Zhang [a], Hong-Yan Lin [a], Zi-Wei Cui [a]

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

Cu(1)-O(1)	1.998(3)	Cu(3)-O(4)	1.998(3)
Cu(1)-O(2)	2.316(3)	Cu(3)-O(4W)	1.957(3)
Cu(1)-N(1)	1.948(4)	Cu(3)-N(5)	1.967(4)
Cu(1)-O(1W)	1.949(4)	Cu(3)-N(6)	1.939(3)
Cu(1)-N(2)	1.946(4)	Cu(3)-O(5W)	2.549(3)
Cu(2)-O(3)	2.012(3)	Cu(4)-O(5W)	1.976(3)
Cu(2)-O(2W)	2.304(3)	Cu(4)-O(5)	1.943(3)
Cu(2)-N(3)	1.960(4)	Cu(4)-N(8)	1.928(4)
Cu(2)-N(4)	1.948(4)	Cu(4)-N(7)	1.920(4)
Cu(2)-O(5W)	1.963(4)	O(4W)-Cu(3)-O(4)	86.83(13)
O(4W)-Cu(3)-N(5)	167.63(14)	N(5)-Cu(3)-O(4)	81.78(14)
N(6)-Cu(3)-O(4)	170.10(14)	N(6)-Cu(3)-O(4W)	94.38(15)
N(6)-Cu(3)-N(5)	97.67(15)	O(5)-Cu(4)-O(5W)	82.76(13)
N(8)-Cu(4)-O(5W)	165.19(14)	N(8)-Cu(4)-O(5)	83.00(14)
N(7)-Cu(4)-O(5W)	95.92(14)	N(7)-Cu(4)-O(5)	173.73(14)
N(7)-Cu(4)-N(8)	98.67(15)	N(1)-Cu(1)-O(1)	81.66(15)
O(1)-Cu(1)-O(2)	99.93(12)	N(1)-Cu(1)-O(2)	93.25(14)
N(1)-Cu(1)-O(1W)	164.65(16)	O(1W)-Cu(1)-O(1)	84.81(15)
O(1W)-Cu(1)-O(2)	96.19(13)	N(2)-Cu(1)-O(1)	167.05(15)
N(2)-Cu(1)-O(2)	93.00(14)	N(2)-Cu(1)-N(1)	98.54(17)
N(2)-Cu(1)-O(1W)	93.03(17)	O(3)-Cu(2)-O(2W)	107.32(14)
N(3)-Cu(2)-O(3)	161.37(15)	N(3)-Cu(2)-O(2W)	91.31(14)
N(3)-Cu(2)-O(3W)	94.73(17)	N(4)-Cu(2)-O(3)	81.30(16)
N(4)-Cu(2)-O(2W)	91.21(15)	N(4)-Cu(2)-N(3)	98.15(17)
N(4)-Cu(2)-O(3W)	166.38(16)	O(3W)-Cu(2)-O(3)	85.09(16)
O(3W)-Cu(2)-O(2W)	92.90(15)		

Symmetry code for **1**: #1 -x, -y+1, -z+1

Table S2 The detailed data for hydrogen bonds for complex **1**

O(4W)-H(4WA)	0.8528	O(2W)-H(2WA)	0.8672
O(4W)-H(4WB)	0.8527	O(2W)-H(2WB)	0.8663
O(1W)-H(1WA)	0.8512	O(1W)-H(1WB)	0.8510
H(4WA)-O(4W)-H(4WB)	104.3	H(2WA)-O(2W)-H(2WB)	103.7
H(1WA)-O(1W)-H(1WB)	104.5	H(3WA)-O(3W)-H(3WB)	98.5
H(5WA)-O(5W)-H(5WB)	104.5	H(6WA)-O(6W)-H(6WB)	104.5

Table S3 Bond lengths [Å] and angles [°] for complex **2**

Co(1)-O(2)	2.060(3)	Co(1)-O(1)	2.151(3)
Co(1)-O(3)#3	2.115(3)	Co(1)-N(1)	2.088(4)
Co(1)-O(1W)	2.118(3)	Co(1)-N(2)#3	2.083(4)
N(2)#3-Co(1)-O(1)	95.36(14)	N(2)#3-Co(1)-N(1)	169.87(15)
O(2)-Co(1)-O(3)#3	168.58(13)	O(2)-Co(1)-O(1W)	84.99(12)
O(2)-Co(1)-O(1)	87.78(13)	O(2)-Co(1)-N(1)	90.65(13)
O(2)-Co(1)-N(2)#3	95.94(13)	O(3)#3-Co(1)-O(1W)	85.68(14)
O(3)#3-Co(1)-O(1)	102.13(14)	O(1W)-Co(1)-O(1)	170.71(13)
N(1)-Co(1)-O(3)#3	97.03(13)	N(1)-Co(1)-O(1W)	97.05(14)
N(1)-Co(1)-O(1)	77.16(14)	N(2)#3-Co(1)-O(3)#3	77.67(13)
N(2)#3-Co(1)-O(1W)	91.20(14)		

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

Table S4 The detailed data for hydrogen bonds for complex **2**

O(1W)-H(1WA)	0.8629	O(1W)-H(1WB)	0.8627
H(1WA)-O(1W)-H(1WB)	103.7		

Table S5 Bond lengths [Å] and angles [°] for complex **3**

Co(1)-O(3)	2.053(3)	Co(1)-O(2)#2	2.126(3)
Co(1)-O(1)	2.076(3)	Co(1)-O(1W)	2.075(3)
Co(1)-N(3)#2	2.136(3)	Co(1)-N(1)	2.187(4)
Co(2)-O(5)	2.406(2)	Co(2)-O(5)#3	2.406(2)
Co(2)-O(2W)	2.058(3)	Co(2)-O(2W)#3	2.058(3)
Co(2)-O(3W)	2.031(3)	Co(2)-O(3W)#3	2.031(3)
O(3)-Co(1)-O(2)#2	91.82(11)	O(3)-Co(1)-O(1)	171.72(11)
O(3)-Co(1)-O(1W)	87.76(12)	O(3)-Co(1)-N(3)#2	89.03(12)
O(3)-Co(1)-N(1)	95.11(12)	O(2)#2-Co(1)-N(3)#2	76.77(11)

O(2)#2-Co(1)-N(1)	98.26(12)	O(1)-Co(1)-O(2)#2	90.79(12)
O(1)-Co(1)-N(3)#2	99.22(12)	O(1)-Co(1)-N(1)	76.73(12)
O(1W)-Co(1)-O(2)#2	173.37(12)	O(1W)-Co(1)-O(1)	90.54(13)
O(1W)-Co(1)-N(3)#2	99.22(12)	O(1W)-Co(1)-N(1)	88.37(13)
N(3)#2-Co(1)-N(1)	173.66(13)	O(5)-Co(2)-O(5)#3	180.0
O(2W)-Co(2)-O(5)#3	95.47(10)	O(2W)#3-Co(2)-O(5)#3	84.53(10)
O(2W)#3-Co(2)-O(5)	95.47(10)	O(2W)-Co(2)-O(5)	84.53(10)
O(2W)-Co(2)-O(2W)#3	180.0	O(2W)#3-Co(2)-O(3W)#3	88.33(13)
O(2W)#3-Co(2)-O(3W)	91.67(13)	O(2W)-Co(2)-O(3W)#3	91.67(13)
O(2W)-Co(2)-O(3W)	88.33(13)	O(3W)-Co(2)-O(5)#3	88.26(10)
O(3W)-Co(2)-O(5)	91.74(10)	O(3W)#3-Co(2)-O(5)	88.26(10)
O(3W)#3-Co(2)-O(5)#3	88.26(10)	O(3W)-Co(2)-O(3W)#3	180.0

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

Table S6 The detailed data for hydrogen bonds for complex **3**

O(3W)-H(3WA)	0.8515	O(3W)-H(3WB)	0.8514
O(2W)-H(2WA)	0.8499	O(2W)-H(2WB)	0.8501
O(1W)-H(1WA)	0.8502	O(1W)-H(1WB)	0.8501
H(3WA)-O(3W)-H(3WB)	104.4	H(2WA)-O(2W)-H(2WB)	104.5
H(1WA)-O(1W)-H(1WB)	104.5		

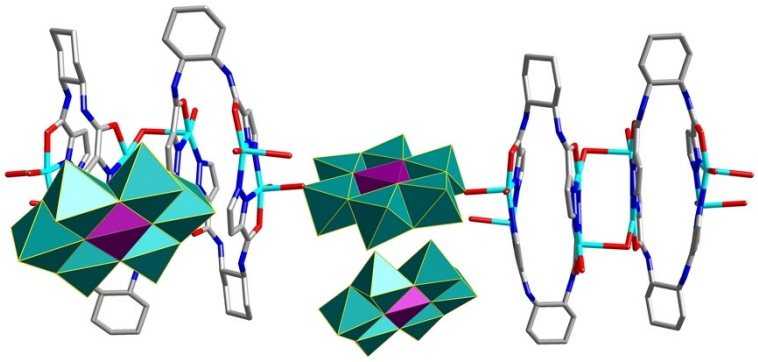

Fig. S1 Schematic diagram of two lattice POMs structure in complex **1**.

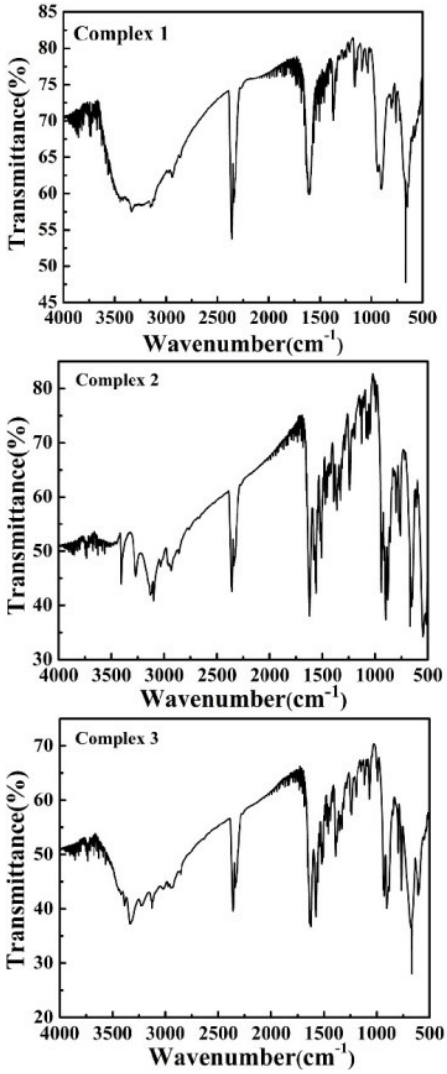

Fig. S2 The IR spectra of complexes **1-3**.