Supporting Information

Metal nuclearity affects network connectivity: a series of highly connected metal-organic frameworks based on polynuclear metal clusters as secondary building units

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Luminescent properties

The solid state photoluminescence spectra of compounds **3-5** with d^{10} metal center and free ligand H_4aobtc (conjugated π system) were employed at room temperature under the same conditions (Fig. S7 and S8). The free ligand H_4aobtc displays emissions at 475 and 528 nm upon excitation at 360 nm. The photoluminescence spectra of compounds **3**−**5** are similar to H_4aobtc and emission maxima are 474 and 528 nm for **3**, 475 and 527 nm for **4**, 475 and 528 nm for **5** upon excitation at 360 nm, respectively. The emissions of compounds **3-5** may be assigned to intraligand transitions of H_4aobtc, because the corresponding ligand also shows similar emission.

Table S1 Selected bond lengths (Å) and angles (°) for compounds **1**-**7**.

Compound **1**

Co(1)-O(1)	2.0284(19)	Co(3)-O(3)#6	2.214(2)
Co(1)-O(8)#1	2.1091(19)	Co(3)-O(4)#6	2.082(2)
Co(1)-O(11) #2	2.069(2)	Co(3)-O(5)#4	2.031(2)
Co(1)-O(14)#3	2.2360(19)	Co(3)-O(8)#5	2.1470(19)
Co(1)-Ow1	2.1898(18)	Co(3)-O(14)	2.1409(19)
Co(1)-N(4)	2.155(2)	Co(3)-O(16)	2.0002(18)
Co(2)-O(6)#4	2.106(2)	Co(4)-Ow2#7	2.133(3)
Co(2)-O(7)	2.052(2)	Co(4)-Ow2	2.128(3)
Co(2)-O(13)	2.0943(18)	Co(4)-Ow3#7	2.056(2)
Co(2)-Ow1	2.2055(17)	Co(4)-Ow3	2.056(2)
Co(2)-O(16)#5	2.1231(19)	Co(4)-N(5)#7	2.202(2)
Co(2)-O(16)	2.0296(19)	Co(4)-N(5)	2.201(2)
O(1)-Co(1)-O(8)#2	170.29(8)	O(4)#6-Co(3)-O(3)#6	61.12(8)
O(1)-Co(1)-O(11) #3	95.25(8)	O(4)#6-Co(3)-O(8)#5	83.89(8)
O(1)-Co(1)-O(14)#1	91.16(8)	O(4)#6-Co(3)-O(14)	103.27(8)
O(1)-Co(1)-Ow1	92.16(8)	O(5)#4-Co(3)-O(3)#6	95.48(9)
O(1)-Co(1)-N(4)	93.17(8)	O(5)#4-Co(3)-O(4)#6	88.33(9)
O(8)#2-Co(1)-O(14)#12	80.91(7)	O(5)#4-Co(3)-O(8)#5	168.32(8)
O(8)#2-Co(1)-Ow1	81.72(7)	O(5)#4-Co(3)-O(14)	91.09(9)
O(8)#2-Co(1)-N(4)	92.91(8)	O(8)#5-Co(3)-O(3)#6	88.39(8)
O(11) #3-Co(1)-O(8)#2	92.15(8)	O(14)-Co(3)-O(3)#6	162.75(8)
O(11) #3-Co(1)-O(14)#1	171.59(7)	O(14)-Co(3)-O(8)#5	82.28(7)
O(11) #3-Co(1)-OW(1)	88.64(8)	O(16)-Co(3)-O(3)#6	96.96(8)
O(11) #3-Co(1)-N(4)	91.52(9)	O(16)-Co(3)-O(4)#6	157.92(8)
Ow1-Co(1)-O(14)#1	85.66(7)	O(16)-Co(3)-O(5)#4	96.94(8)
N(4)-Co(1)-O(14)#1	93.57(8)	O(16)-Co(3)-O(8)#5	93.51(7)
N(4)-Co(1)-Ow1	174.63(8)	O(16)-Co(3)-O(14)	98.07(7)
O(6)#4-Co(2)-Ow2	85.64(7)	Ow2-Co(4)-Ow2#7	180.00(5)
O(6)#4-Co(2)-O(16) #5	171.24(7)	Ow2#7-Co(4)-N(5)	87.28(10)
O(7)-Co(2)-O(6)#	94.06(9)	Ow2-Co(4)-N(5)#7	87.28(10)

O(7) #1-Co(2)-O(13)#4	87.75(8)	Ow2-Co(4)-N(5)	92.72(10)
O(7) #1-Co(2)-Ow2	87.59 (7)	Ow2#7-Co(4)-N(5) #7	92.72(10)
O(7) -Co(2)-O(16) #5	87.30(8)	Ow3#7-Co(4)-Ow2	92.25(11)
O(13)-Co(2)-O(6)#4	86.61(8)	Ow3-Co(4)-Ow2	87.75(11)
O(13)-Co(2)-Ow2	170.65(8)	Ow3#7-Co(4)-Ow2#7	87.75(11)
O(13)-Co(2)-O(16) #5	84.80(8)	Ow3-Co(4)-Ow2#7	92.25(11)
O(16)-Co(2)-O(6)#4	96.93(8)	Ow3-Co(4)-Ow3	180.00(11)
O(16)-Co(2)-O(7)	169.00(8)	Ow3-Co(4)-N(5)	90.70(10)
O(16)-Co(2)-O(13)	92.98(8)	Ow3#8-Co(4)-N(5)#7	89.30(10)
O(16)#5-Co(2)-Ow2	103.07(7)	Ow3#7-Co(4)-N(5)	89.30(10)
O(16)-Co(2)-Ow2	93.14(7)	Ow3#7-Co(4)-N(5)#7	90.70(10)
O(16)#5-Co(2)-O(16)	81.85(9)	N(5)#8-Co(4)-N(5)	180.0

Compound **2**

Ni(1)-O(2)#1	2.092(2)	Ni(3)-O(1)#1	2.079(2)
Ni(1)-O(2)#2	2.092(2)	Ni(3)-O(4)#3	2.036(2)
Ni(1)-O(3)	2.167(2)	Ni(3)-O(6)	1.998(2)
Ni(1)-O(3)#3	2.167(2)	Ni(3)-O(8)	2.093(2)
Ni(1)-O(6)#3	2.040(2)	Ni(3)-O(9)#4	2.075(2)
Ni(1)-O(6)	2.040(2)	Ni(3)-N(1)	2.085(3)
Ni(2)-O(6)#3	2.029(2)	Ni(4)-Ow2	2.064(3)
Ni(2)-O(6)	2.029(2)	Ni(4)-Ow3	2.051(2)
Ni(2)-O(7)#3	2.024(2)	Ni(4)-Ow3#5	2.051(2)
Ni(2)-O(7)	2.024(2)	Ni(4)-Ow4	2.113(4)
Ni(2)-Ow1#3	2.136(3)	Ni(4)-N(2)	2.085(2)
Ni(2)-Ow1	2.136(3)	Ni(4)-N(2)#5	2.085(2)
O(2)#1 -Ni(1) -O(2)#2	165.65(13)	O(1)#1 -Ni(3) -O(8)	87.93(10)
O(2)#1 -Ni(1) -O(3)	84.26(8)	O(1)#1 -Ni(3) -N(1)	88.10(10)
O(2)#2 -Ni(1) -O(3)	86.29(9)	O(4)#3 -Ni(3) -O(1)#1	88.84(11)
O(2)#2 -Ni(1) -O(3)#3	84.26(9)	O(4)#3 -Ni(3) -O(8)	175.63(10)
O(2)#1 -Ni(1) -O(3)#3	86.29(9)	O(4)#3 -Ni(3) -O(9)#4	92.53(12)

O(3)#3 -Ni(1) -O(3)	97.50(11)	O(4)#3 -Ni(3) -N(1)	86.41(9)
O(6)#3 -Ni(1) -O(2)#2	93.00(9)	O(6) -Ni(3) -O(1)#1	93.69(9)
O(6)#3 -Ni(1) -O(2)#1	97.85(9)	O(6) -Ni(3) -O(4)#3	89.76(9)
O(6) -Ni(1) -O(2)#1	93.00(9)	O(6) -Ni(3) -O(8)	93.38(9)
O(6) -Ni(1) -O(2)#2	97.85(9)	O(6) -Ni(3) -O(9)#4	93.48(10)
O(6) -Ni(1) -O(3)#3	90.50(8)	O(6) -Ni(3) -N(1)	175.74(10)
O(6)#3 -Ni(1) -O(3)#3	171.35(9)	O(9)#4 -Ni(3) -O(1)#1	172.71(10)
O(6)#3 -Ni(1) -O(3)	90.50(8)	O(9)#4 -Ni(3) -O(8)	90.32(11)
O(6) -Ni(1) -O(3)	171.34(9)	O(9)#4 -Ni(3) -N(1)	84.84(10)
O(6) -Ni(1) -O(6)#3	81.73(12)	N(1) -Ni(3) -O(8)	90.54(9)
O(6)#3 -Ni(2) -O(6)	82.25(12)	Ow2 -Ni(4) -Ow4	180.0
O(6)#3 -Ni(2) -Ow1	95.09(9)	Ow2 -Ni(4) -N(2)	93.23(8)
O(6) -Ni(2) -Ow1#3	95.09(9)	Ow2 -Ni(4) -N(2)#5	93.23(8)
O(6)#3 -Ni(2) -Ow1#3	85.84(10)	Ow3#5 -Ni(4) -Ow2	90.01(8)
O(6) -Ni(2) -Ow1	85.84(10)	Ow3 -Ni(4) -Ow2	90.01(8)
O(7) #3 -Ni(2) -O(6)	176.65(9)	Ow3#5 -Ni(4) -Ow3	179.97(16)
O(7)#3 -Ni(2) -O(6) #3	95.92(9)	Ow3 -Ni(4) -Ow4	89.99(8)
O(7) -Ni(2) -O(6)#3	176.65(9)	Ow3#5 -Ni(4) -Ow4	89.99(8)
O(7) -Ni(2) -O(6)	95.92(9)	Ow3 -Ni(4) -N(2)	85.32(10)
O(7) -Ni(2) -O(7)#3	86.05(15)	Ow3 -Ni(4) -N(2)#5	94.68(10)
O(7) -Ni(2) -Ow1#3	91.55(11)	Ow3#5 -Ni(4) -N(2)	94.68(10)
O(7) -Ni(2) -Ow1	87.55(11)	Ow3#5 -Ni(4) -N(2)#5	85.32(10)
O(7)#3 -Ni(2) -Ow1#3	87.55(11)	N(2) -Ni(4) -Ow4	86.77(8)
O(7)#3 -Ni(2) -Ow1	91.55(11)	N(2)#5 -Ni(4) -Ow4	86.77(8)
Ow1 -Ni(2) -Ow1#3	178.77(15)	N(2) -Ni(4) -N(2)#5	173.55(16)

Compound **3**

Zn(1)-O(1)	2.005(2)	Zn(2)-O(2)#4	2.010(2)
Zn(1)-O(4)#2	2.030(2)	Zn(2)-O(4)#2	2.222(2)
Zn(1)-O(5)#3	1.990(2)	Zn(2)-O(4)#5	2.222(2)
Zn(1)-O(7)#1	2.367(3)	Zn(2)-O(6)#6	2.079(2)

Zn(1)-O(8)#1	2.037(3)	Zn(2)-O(6)#3	2.079(2)
Zn(2)-O(2)	2.010(2)		
O(1)-Zn(1)-O(4)#2	114.34(10)	O(2)-Zn(2)-O(4)#5	88.35(9)
O(1)-Zn(1)-O(7)#1	90.01(13)	O(2)-Zn(2)-O(4)#2	88.42(10)
O(1)-Zn(1)-O(8)#1	105.87(11)	O(2)#4-Zn(2)-O(6)#6	96.17(10)
O(4)#2-Zn(1)-O(7)#1	90.84(10)	O(2)#4-Zn(2)-O(6)#3	83.83(10)
O(4)#2-Zn(1)-O(8)#1	129.14(10)	O(2)-Zn(2)-O(6)#3	96.17(10)
O(5)#3-Zn(1)-O(1)	103.39(11)	O(2)-Zn(2)-O(6)#6	83.83(10)
O(5)#3-Zn(1)-O(4)#2	98.58(10)	O(4)#2-Zn(2)-O(4)#5	180.0
O(5)#3-Zn(1)-O(7)#1	158.51(12)	O(6)#6-Zn(2)-O(4)#5	87.84(9)
O(5)#3-Zn(1)-O(8)#1	101.12(10)	O(6)#3-Zn(2)-O(4)#5	92.16(9)
O(8)#1-Zn(1)-O(7)#1	58.55(10)	O(6)#3-Zn(2)-O(4)#2	87.84(9)
O(2)#4-Zn(2)-O(2)#4	180.0	O(6)#6-Zn(2)-O(4)#2	92.16(9)
O(2)#4-Zn(2)-O(4)#2	91.65(9)	O(6)#6-Zn(2)-O(6)#3	180.0
O(2)#4-Zn(2)-O(4)#5	88.35(9)		

Compound **4**

Zn(1)-O(1)	1.994(19)	Zn(2)-O(2)#4	2.0539(19)
Zn(1)-O(3)#1	2.425(2)	Zn(2)-O(5)#3	2.020(18)
Zn(1)-O(4)#1	2.016(2)	Zn(2)-O(5)#6	2.020(18)
Zn(1)-O(6)#2	1.994(19)	Zn(2)-O(8)#5	2.238(18)
Zn(1)-O(8)#3	2.013(18)	Zn(2)-O(8)#3	2.238(18)
Zn(2)-O(2)	2.0534(17)		
O(1)-Zn(1)-O(3)#1	161.66(8)	O(2)#4-Zn(2)-O(8)#2	91.58(7)
O(1)-Zn(1)-O(4)#1	104.54(8)	O(2)-Zn(2)-O(8)#2	88.42(7)
O(1)-Zn(1)-O(8)#2	97.956(8)	O(5)#3-Zn(2)-O(2)	96.05(8)
O(4)#1-Zn(1)-O(3)#1	58.10(8)	O(5)#6-Zn(2)-O(2)	83.95(8)
O(6)#3-Zn(1)-O(1)	102.11(9)	O(5)#3-Zn(2)-O(2)#4	83.95(8)
O(6)#3-Zn(1)-O(3)#1	89.53(9)	O(5)#6-Zn(2)-O(2)#4	96.05(8)
O(6)#3-Zn(1)-O(4)#1	106.22(9)	O(5)#6-Zn(2)-O(5)#3	180.0
O(6)#3-Zn(1)-O(8)#2	118.89(8)	O(5)#6-Zn(2)-O(8)#5	88.59(8)
O(8)#2-Zn(1)-O(3)#1	88.51(9)	O(5)#6-Zn(2)-O(8)#2	91.38(8)
O(8)#2-Zn(1)-O(4)#1	123.32(8)	O(5)#3-Zn(2)-O(8)#5	91.38(8)
O(2)-Zn(2)-O(2)#4	180.0	O(5)#3-Zn(2)-O(8)#2	88.62(8)

O(2)#4 -Zn(2) -O(8)#5	88.42(7)	O(8)#5 -Zn(2) -O(8)#2	180.00(8)
O(2) -Zn(2) -O(8)#5	91.58(7)		

Compound **5**

Cd(1)-O(1)	2.252(3)	Cd(2)-O(2)#4	2.241(4)
Cd(1)-O(4)#2	2.267(3)	Cd(2)-O(4)#2	2.297(3)
Cd(1)-O(5)#3	2.192(3)	Cd(2)-O(4)#5	2.297(3)
Cd(1)-O(7)#1	2.305(3)	Cd(2)-O(6)#6	2.242(3)
Cd(1)-O(8)#1	2.357(3)	Cd(2)-O(6)#3	2.242(3)
Cd(2)-O(2)	2.241(4)		
O(1) -Cd(1) -O(4)#2	115.76(12)	O(2) -Cd(2) -O(4)#2	81.06(13)
O(1) -Cd(1)- O(7)#1	105.16(15)	O(2) -Cd(2) -O(4)#5	98.94(13)
O(1) -Cd(1) -O(8)#1	91.76(15)	O(2) -Cd(2) -O(6)#3	92.33(15)
O(4)#2 -Cd(1)- O(7)#1	132.82(13)	O(2) -Cd(2)- O(6)#6	87.67(15)
O(4)#2 -Cd(1) -O(8)#1	98.06(13)	O(2)#4 -Cd(2) -O(6)#3	87.67(15)
O(5)#3 -Cd(1) -O(1)	100.37(15)	O(2)#4 -Cd(2) -O(6)#6	92.33(15)
O(5)#3 -Cd(1) -O(4)#2	97.07(13)	O(4)#2 -Cd(2) -O(4)#5	180.0
O(5)#3 -Cd(1) -O(7)#1	97.69(12)	O(6)#6 -Cd(2) -O(4)#5	89.06(12)
O(5)#3 -Cd(1) -O(8)#1	153.14(12)	O(6)#6 -Cd(2) -O(4)#2	90.94(12)
O(7)#1 -Cd(1) -O(8)#1	55.79(12)	O(6)#3 -Cd(2) -O(4)#5	90.94(12)
O(2) -Cd(2) -O(2)#4	180.0	O(6)#3 -Cd(2) -O(4)#2	89.06(12)
O(2)#4 -Cd(2) -O(4)#5	81.06(13)	O(6)#6 -Cd(2) -O(6)#3	180.0
O(2)#4 -Cd(2) -O(4)#2	98.94(13)		

Compound **6**

Co(1)-O(2) #2	1.994(2)	Co(2) -O(1) #2	2.0605(19)
Co(1)-O(3)#6	2.345(2)	Co(2) -O(6)#3	2.021(2)
Co(1)-O(4) #6	2.032(2)	Co(2) -O(6)	2.021(2)
Co(1)-O(7)	2.017(2)	Co(2) -O(8)#4	2.209(2)
Co(1)-O(8)#5	2.034(2)	Co(2) -O(8)#4	2.209(2)
Co(2)-O(1) #1	2.0605(19)		
O(1) #2-Co(2) -O(1)#3	180	O(6) -Co(2) -O(8)#4	91.49(8)

O(1)#2-Co(2)-O(8)#4	90.12(8)	O(8)#4-Co(2)-O(8)#5	180.0
O(1)#3-Co(2)-O(8)#4	89.88(12)	O(2)#2-Co(1)-O(3)#7	163.82(9)
O(1)#3-Co(2)-O(8)#5	90.12(8)	O(2)#2-Co(1)-O(4)#7	105.08(9)
O(1)#2-Co(2)-O(8)#5	89.88(8)	O(2)#2-Co(1)-O(7)	101.67(10)
O(6)#6-Co(2)-O(1)#2	84.48(9)	O(2)#2-Co(1)-O(8)#5	98.74 (9)
O(6) -Co(2) -O(1)#2	95.52(9)	O(4)#7-Co(1)-O(3)#7	59.41(8)
O(6)-Co(2)-O(1)#3	84.48(9)	O(4)#7-Co(1)-O(8)#5	125.95(9)
O(6)#6-Co(2)-O(1)#3	95.52(9)	O(7)-Co(1)-O(3)#7	87.83(10)
O(6)-Co(2)-O(6)#6	180.0	O(7)-Co(1)-O(4)#7	105.08(10)
O(2)-Co(2)-O(8)#5	88.51(8)	O(7)-Co(1)-O(8)#5	116.61(9)
O(6)#6-Co(2)-O(8)#5	91.50(8)	O(8)#5-Co(1)-O(3)#7	88.40(9)
O(6)#6-Co(2)-O(8)#4	88.50(8)		

Compound **7**

Mn(1)-O(1)	2.132(2)	Mn(2)-O(2)	2.131(2)
Mn(1)-O(4)#2	2.1667(19)	Mn(2)-O(4)#2	2.2319(18)
Mn(1)-O(5)#1	2.193(2)	Mn(2)-O(4)#5	2.1319(18)
Mn(1)-O(6)#1	2.266(2)	Mn(2)-O(7)#6	2.1323(19)
Mn(1)-O(8)#3	2.076(2)	Mn(2)-O(7)#3	2.1323(19)
Mn(2)-O(2)#4	2.131(2)		
O(1)-Mn(1)-O(4)#2	118.56(9)	O(2)#4-Mn(2)-O(4)#2	97.08(9)
O(1)-Mn(1)-O(5)#1	103.39(10)	O(2)-Mn(2)-O(4)#5	97.08(9)
O(1)-Mn(1)-O(6)#1	92.76(10)	O(2)-Mn(2)-O(7)#6	86.69(9)
O(4)#2-Mn(1)-O(5)#1	131.68(8)	O(2)#4-Mn(2)-O(7)#3	86.69(9)
O(4)#2-Mn(1)-O(6)#1	94.72(8)	O(2)#4-Mn(2)-O(7)#6	93.31(9)
O(5)#1-Mn(1)-O(6)#1	58.57(8)	O(2)-Mn(2)-O(7)#3	93.31(9)
O(8)#3-Mn(1)-O(1)	99.45(10)	O(4)#2-Mn(2)-O(4)#5	180.0
O(8)#3-Mn(1)-O(4)#2	95.03(8)	O(7)#3-Mn(2)-O(4)#5	91.34(8)
O(8)#3-Mn(1)-O(5)#1	100.93(8)	O(7)#6-Mn(2)-O(4)#5	88.66(8)
O(8)#3-Mn(1)-O(6)#1	158.34(9)	O(7)#3-Mn(2)-O(4)#2	88.66(8)
O(2)-Mn(2)-O(2)#4	180.0	O(7)#6-Mn(2)-O(4)#2	91.34(8)

O(2)#4 -Mn(2) -O(4)#5	82.92(9)	O(7)#6 -Mn(2) -O(7)#3	180.0
O(2) -Mn(2) -O(4)#2	82.92(9)		

[a] Symmetry transformations used to generate equivalent atoms: for **1:** #1 1-x,1-y,-z; #2 -1+x,+y,+z; #3 1+x,+y,1+z; #4 2-x,1-y,1-z; #5 1-x,1-y,1-z; #6 +x,-1+y,+z; #7 -x,1-y,-z; #8 x,-y,-1-z; for **2:** #1 1-x,1-y,-z; #2 1/2+x,+y,-z; #3 3/2-x,1-y,+z; #4 2-x,+y,1/2-z; #5 3/2-x,-y,+z; for **3**: #1 1+x,1+y,1+z; #2 1+x,+y,+z; #3 1+x,+y,1+z; #4 2-x,1-y,2-z; #5 1-x,1-y,1-z; #6 1-x,1-y,2-z; for **4**: #1 +x, 1+y,+z; #2 +x,+y,-1+z; #3 -1+x,+y,-1+z; #4 -x,-y,-1-z; #5 1-x,-y,-z; #6 -x,-y,-z; for **5**: #1 1+x,1+y,1+z; #2 -1+x,-1+y,-1+z; #3 -1+x,+y,+z; #4 -1+x,+y,-1+z; #5 -1-x,1-y,1-z; #6 -x,1-y,1-z; for **6**: #1 -1+x,-1+y,-1+z; #2 -1+x,+y,+z; #3 -1+x,+y,-1+z; #4 -1-x,1-y,-1-z; #5 -x,1-y,-1-z; #6 -x,1-y,-z; for **7**: #1 -1+x,-1+y,-1+z; #2 1+x,1+y,1+z; #3 1+x,+y,+z; #4 1+x,+y,1+z; #5 2-x,1-y,1-z; #6 1-x,1-y,1-z.

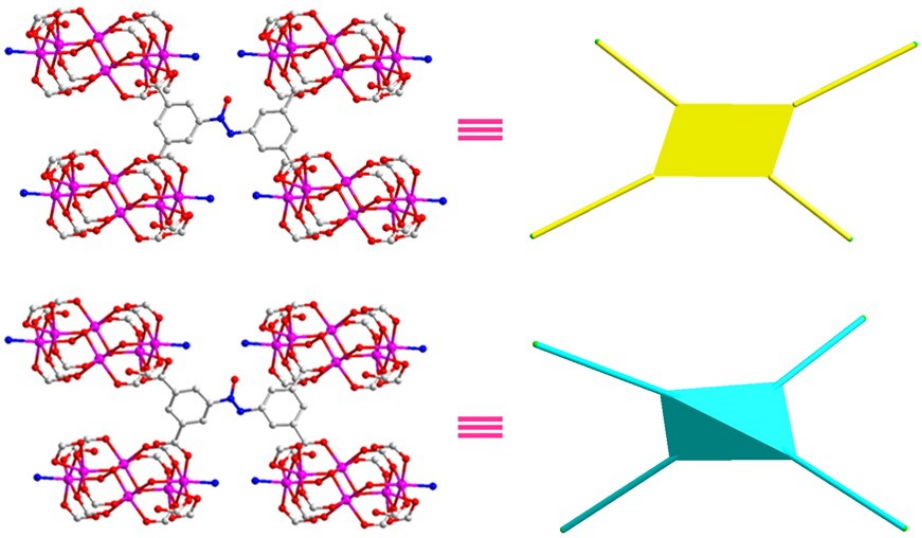

Fig. S1 Two kinds of aobtc ligand are regarded as two kinds of 4-connected nodes in compound **1** (quadrilateral planar node in yellow and tetrahedral node in cyan).

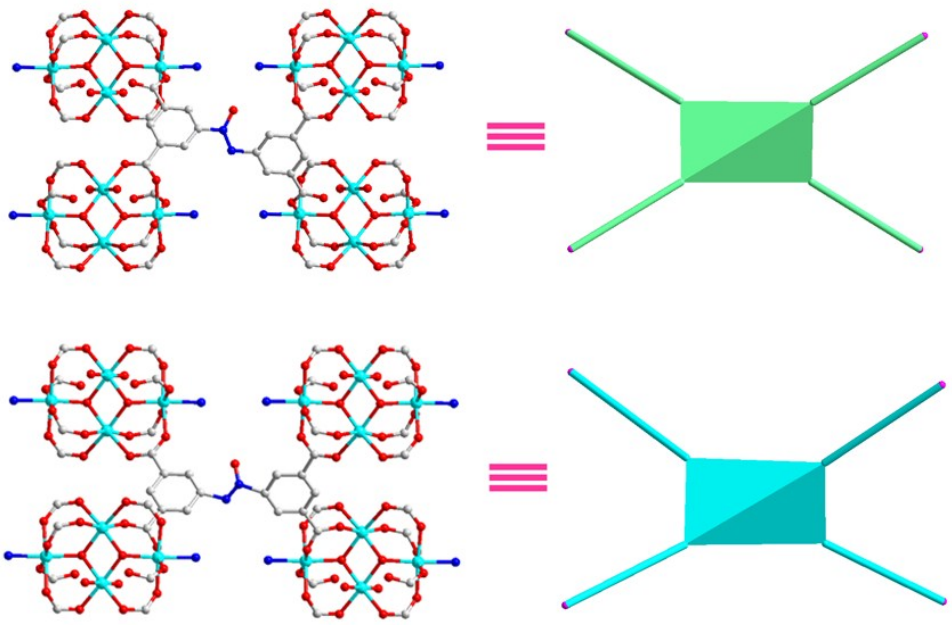

Fig. S2 The two different tetrahedral nodes of aobtc ligand in compound **2**.

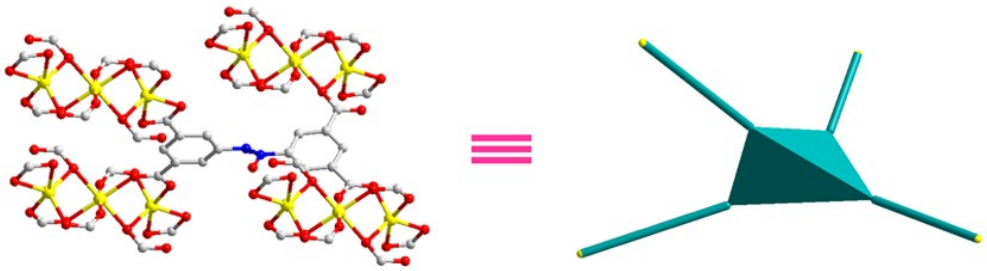

Fig. S3 The tetrahedral node of aobtc ligand in compounds **3-7**.

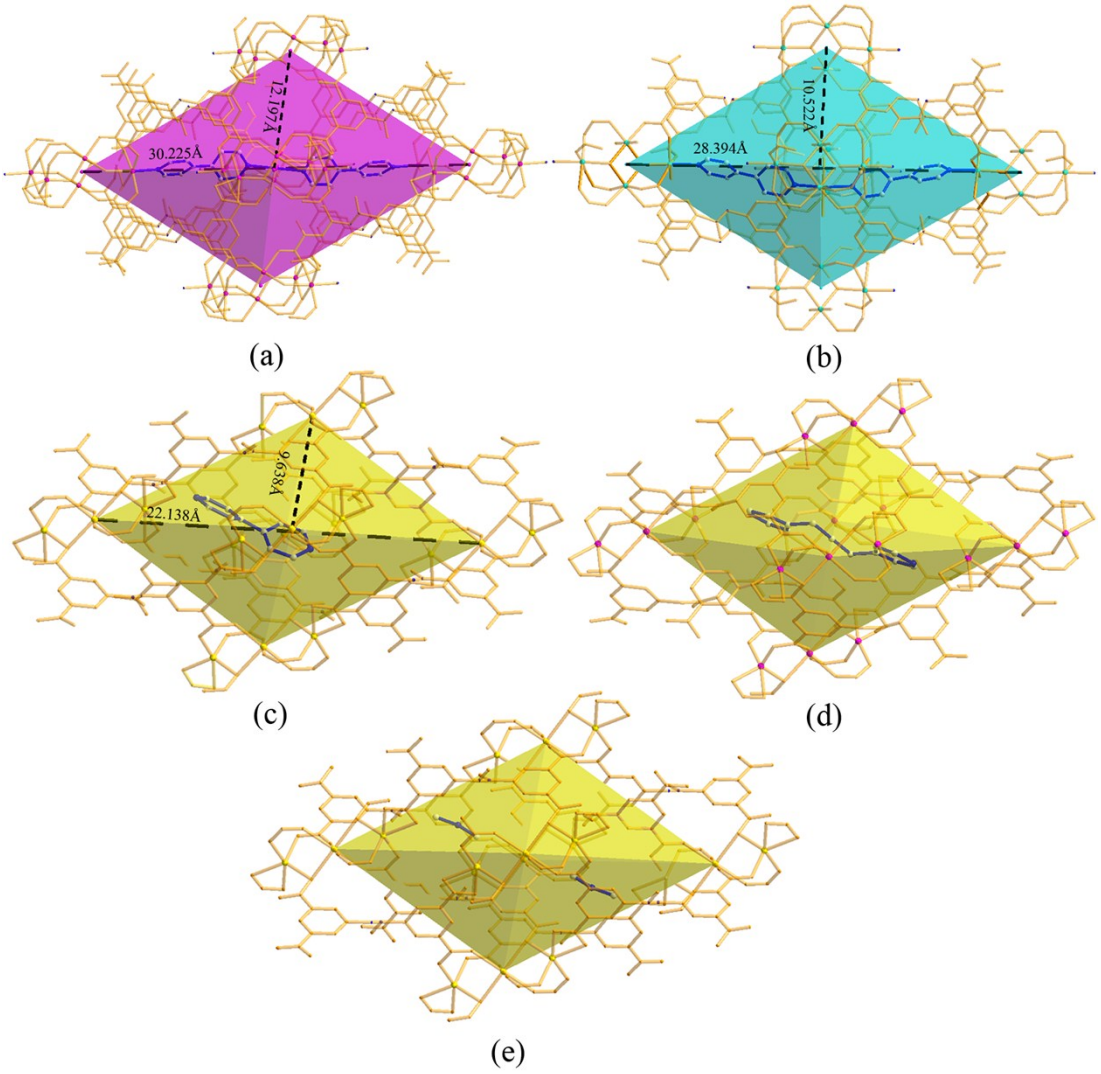

Fig. S4 The octahedral cages of **1**-**7** ((a) for **1**, (b) for **2**, (c) for **3** and **7**, (d) for **4** and **6**, (e) for **5**) built by metal clusters and aobtc ligands, and $[M(bpy)_2]^{2+}$ groups and diprotonate N-donor groups in the cages are highlighted by cerulean lines.

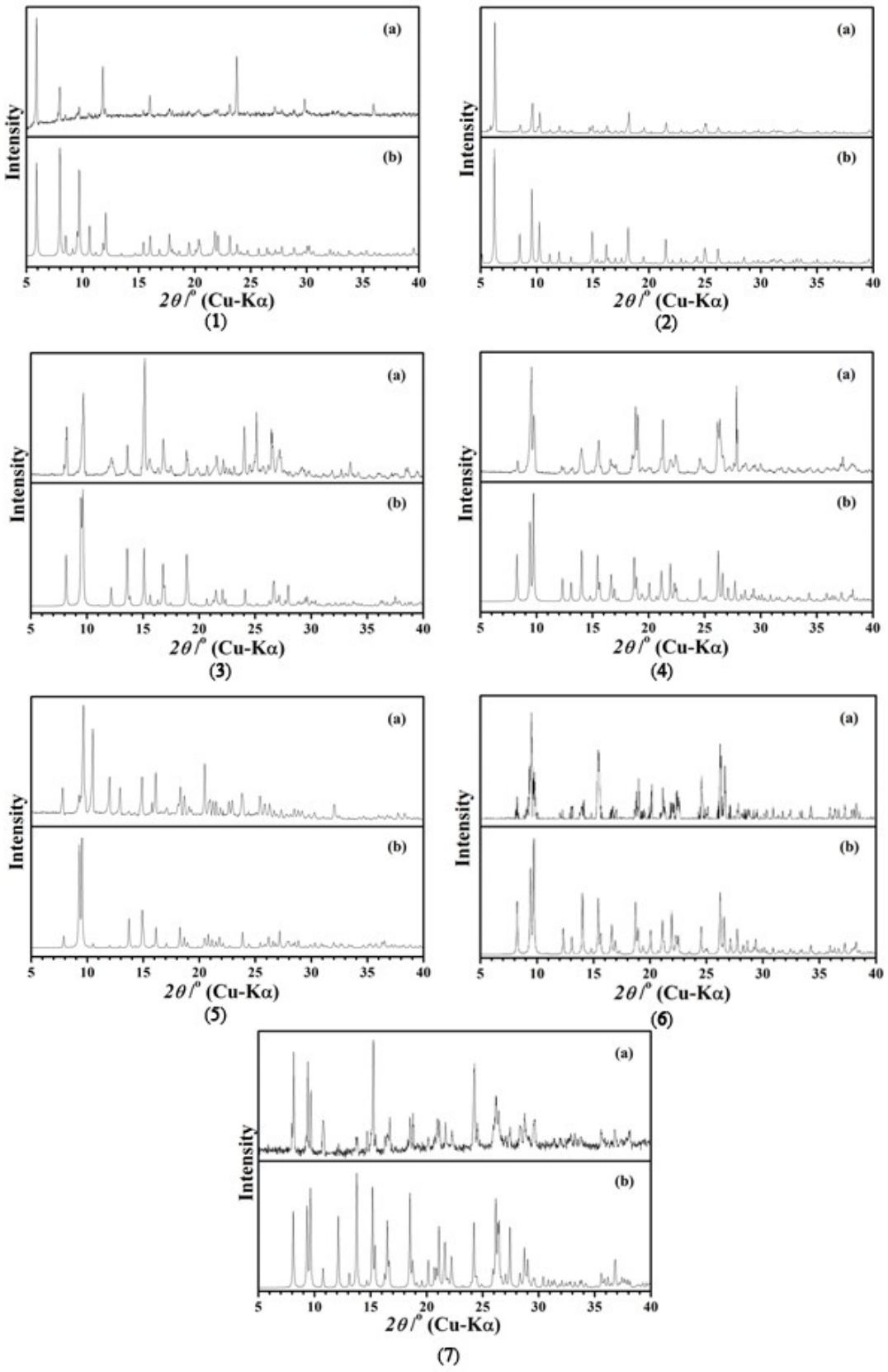

Fig. S5 The PXRD patterns for **1**-**7** ((a): as-synthesized samples, (b): simulated one based on the single-crystal structure).

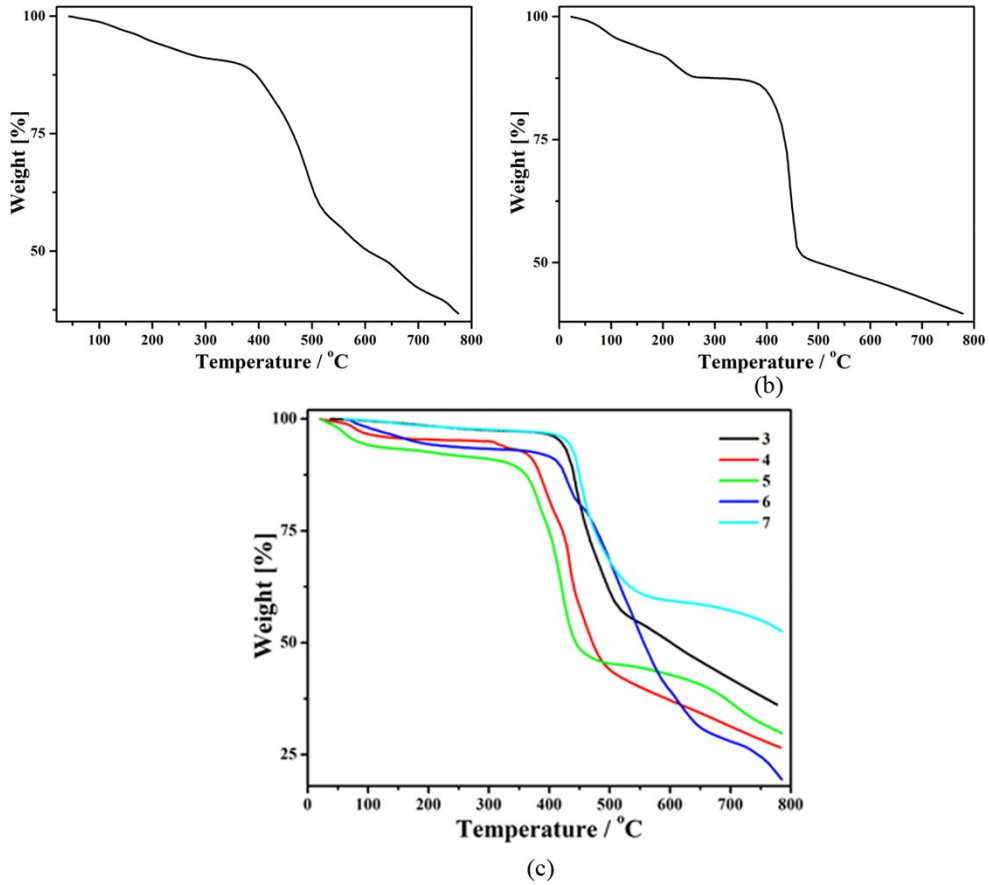

Fig. S6 The TG curves of compounds **1**(a)**, 2**(b)**,** and **3-7**(c).

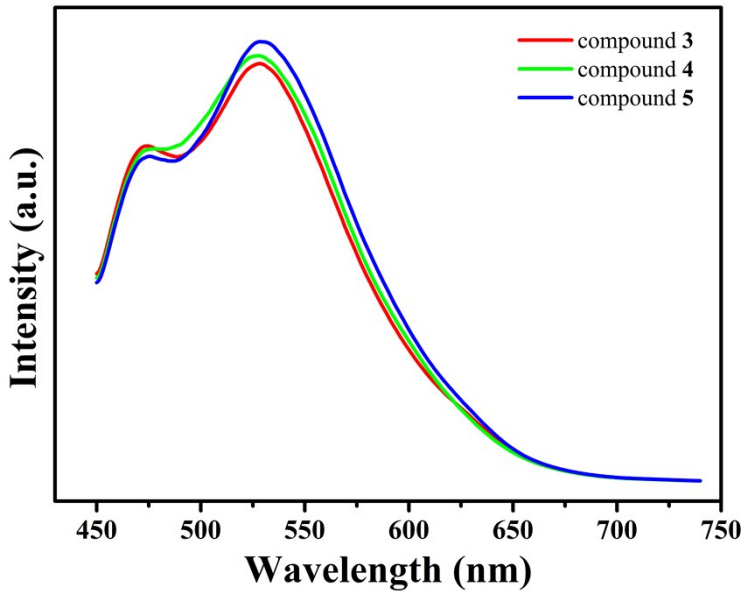

Fig. S7. Solid-state emission spectra of **3-5** at room temperature.

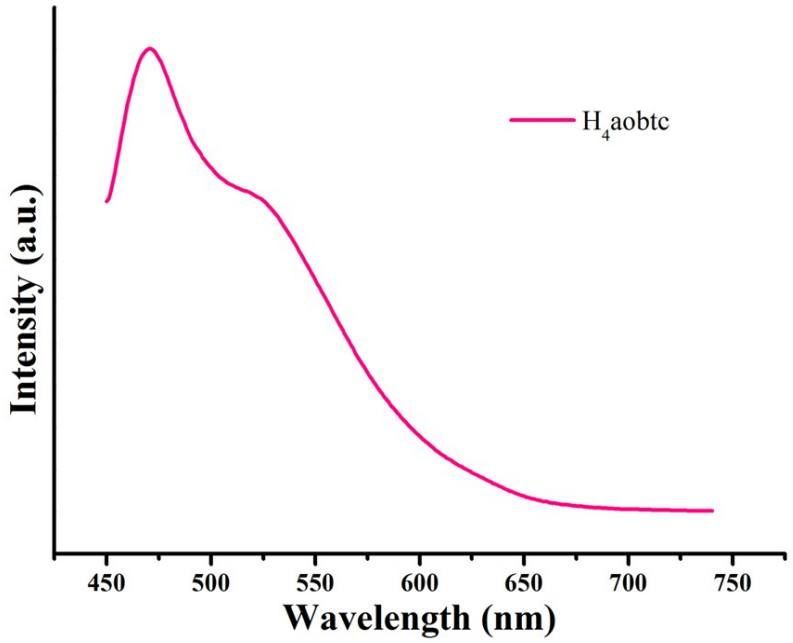

Fig. S8. Solid-state emission spectra of H_4aobtc ligand at room temperature.

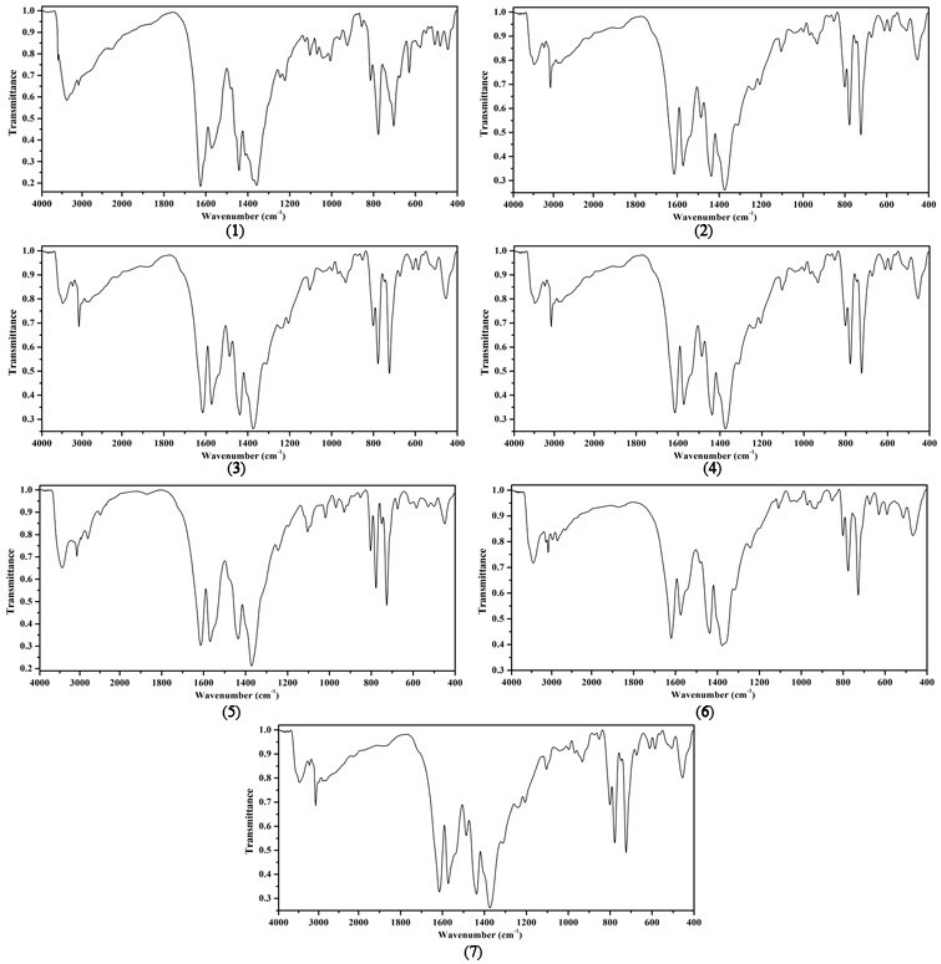

Fig. S9 The IR spectrum of compounds **1-7**.

Topological Analysis by TOPOS 4.0.

Compound **1**: (Sc1:14-conntected $[Co_6(\mu_3\text{-}OH)_2(\mu_2\text{-}OH_2)_2(COO)_{12}]^{2-}$ cluster; V1, Cr1: two kinds of 4-conntected aobtc ligands)

Topology for Sc1

The links to Atom Sc1

Cr1	0.0000	0.5000	0.0000	(0 0 0)	8.282A	1
Cr1	1.0000	0.5000	1.0000	(1 0 1)	8.282A	1
V1	-0.2667	0.1983	0.0321	(0 1 1)	8.500A	1
V1	1.2667	0.8017	0.9679	(1 0 0)	8.500A	1
V1	0.7333	0.1983	0.0321	(1 1 1)	9.327A	1
V1	0.2667	0.8017	0.9679	(0 0 0)	9.327A	1
V1	0.7333	0.1983	1.0321	(1 1 2)	9.894A	1
V1	0.2667	0.8017	-0.0321	(0 0 -1)	9.894A	1
V1	0.7333	1.1983	1.0321	(1 2 2)	10.245A	1
V1	0.2667	-0.1983	-0.0321	(0 -1 -1)	10.245A	1
Cr1	0.0000	0.5000	1.0000	(0 0 1)	11.005A	1
Cr1	1.0000	0.5000	0.0000	(1 0 0)	11.005A	1
Sc1	1.5000	1.5000	2.5000	(1 1 2)	30.225A	1
Sc1	-0.5000	-0.5000	-1.5000	(-1 -1 -2)	30.225A	1

Topology for V1

The links to Atom V1

Sc1	-0.5000	0.5000	0.5000	(-1 0 0)	8.500A	1
Sc1	0.5000	0.5000	0.5000	(0 0 0)	9.327A	1
Sc1	0.5000	0.5000	1.5000	(0 0 1)	9.894A	1
Sc1	0.5000	1.5000	1.5000	(0 1 1)	10.245A	1

Topology for Cr1

The links to Atom Cr1

Sc1	-0.5000	0.5000	-0.5000	(-1 0 -1)	8.282A	1
Sc1	0.5000	0.5000	0.5000	(0 0 0)	8.282A	1
Sc1	0.5000	0.5000	-0.5000	(0 0 -1)	11.005A	1
Sc1	-0.5000	0.5000	0.5000	(-1 0 0)	11.005A	1

Coordination sequences

Sc1:	1	2	3	4	5	6	7	8	9	10
Num	14	40	120	182	346	426	686	772	1140	1220
Cum	15	55	175	357	703	1129	1815	2587	3727	4947

V1:	1	2	3	4	5	6	7	8	9	10
Num	4	42	89	211	282	494	577	891	974	1402

Cum	5	47	136	347	629	1123	1700	2591	3565	4967

Cr1:	1	2	3	4	5	6	7	8	9	10
Num	4	40	90	204	282	484	576	878	972	1386
Cum	5	45	135	339	621	1105	1681	2559	3531	4917

Vertex symbols for selected sublattice

Sc1 Point symbol: $\{4^{30}.5^{26}.6^{31}.7^{4}\}$

Extended point symbol:[4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4(2).4(2).4(2).4(2).4(2).4(2).5.5.5.5.5.5.5.5.5.5.5.5.5.5(2).5(2).5(2).5(2).5(4).5(4).5(4).5(4).5(5).5(5).5(6).5(6).5(7).5(7).6(2).6(2).6(2).6(2).6(3).6(3).6(4).6(4).6(4).6(4).6(5).6(5).6(5).6(5).6(6).6(6).6(6).6(6).6(6).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(9).6(10).6(10).6(11).6(11).7(8).7(8).7(20).7(28)]

V1 Point symbol: $\{4^{6}\}$

Extended point symbol:[4.4(2).4.4(3).4.4(3)]

Cr1 Point symbol: $\{4^{5}.6\}$

Extended point symbol:[4(2).6(20).4(3).4(3).4(3).4(3)]

Point symbol for net: $\{4^{30}.5^{26}.6^{31}.7^{4}\}\{4^{5}.6\}\{4^{6}\}_2$

4,4,14-*c* net with stoichiometry $(4\text{-}c)_2(4\text{-}c)(14\text{-}c)$; 3-nodal net

Compound **2**: (Cr1:10-conntected $[Ni_4(\mu_3\text{-}OH)_2(H_2O)_2(COO)_8]^{2-}$ cluster; Ti1, V1: two kinds of 4-conntected aobtc ligands)

Topology for Ti1

The links to Atom Ti1

Cr1	0.7500	0.0000	0.3747	(1 -1 0)	8.441A	1
Cr1	0.7500	0.5000	0.1253	(0 0 0)	8.441A	1
Cr1	1.2500	0.0000	0.1253	(1 0 0)	9.401A	1
Cr1	1.2500	0.5000	0.3747	(0 1 0)	9.401A	1

Topology for V1

The links to Atom V1

Cr1	0.7500	1.0000	0.8747	(-1 0 1)	8.564A	1
Cr1	0.2500	0.5000	0.8747	(1 1 1)	8.564A	1
Cr1	0.2500	1.0000	1.1253	(0 1 1)	9.112A	1
Cr1	0.7500	0.5000	1.1253	(0 0 1)	9.112A	1

Topology for Cr1

The links to Atom Cr1

Ti1	0.6221	0.7500	0.2500	(1 1 0)	8.441A	1
Ti1	0.8779	0.2500	0.2500	(0 0 0)	8.441A	1
V1	0.5000	0.2500	0.0162	(1 1 1)	8.564A	1
V1	1.0000	0.7500	0.0162	(0 0 1)	8.564A	1
V1	0.5000	0.7500	-0.0162	(0 0 -1)	9.112A	1
V1	1.0000	0.2500	-0.0162	(1 1 -1)	9.112A	1
Ti1	0.3779	0.7500	0.2500	(-1 1 0)	9.401A	1
Ti1	1.1221	0.2500	0.2500	(2 0 0)	9.401A	1
Cr1	0.7500	1.5000	0.1253	(0 1 0)	28.393A	1
Cr1	0.7500	-0.5000	0.1253	(0 -1 0)	28.393A	1

Coordination sequences

Ti1:	1	2	3	4	5	6	7	8	9	10
Num	4	31	64	128	176	290	344	516	568	802
Cum	5	36	100	228	404	694	1038	1554	2122	2924

V1:	1	2	3	4	5	6	7	8	9	10
Num	4	30	64	128	176	288	344	512	568	800
Cum	5	35	99	227	403	691	1035	1547	2115	2915

Cr1:	1	2	3	4	5	6	7	8	9	10
Num	10	30	74	114	202	254	394	450	650	702
Cum	11	41	115	229	431	685	1079	1529	2179	2881

Vertex symbols for selected sublattice

Ti1 Point (Schlafli) symbol: $\{4^6\}$

Extended point symbol:[4.4.4.4.4(2).4(2)]

V1 Point (Schlafli) symbol: $\{4^5.5\}$

Extended point symbol:[4.4.4.4.4(2).5(6)]

Cr1 Point (Schlafli) symbol:$\{4^{10}.5^{18}.6^{12}.7^5\}$

Extended point symbol:[4.4.4.4.4.4.4.4.4(3).4(3).5.5.5.5.5.5.5.5.5.5.5(3).5(3).5(3).5(3).5(3).5(3).5(5).5(5).6(4).6(4).6(4).6(4).6(4).6(5).6(5).6(7).6(7).6(7).6(7).6(7).6(7).7(8).7(8).7(8).7(8).7(8).7(14)]

Point (Schlafli) symbol for net: $\{4^{10}.5^{18}.6^{12}.7^5\}\{4^5.5\}\{4^6\}$

4,10-*c* net with stoichiometry (4-*c*)$_2$(10-*c*); 3-nodal net

Compound **3**: (Ti1:8-conntected $[Zn_3(COO)_8]^{2-}$ cluster; Sc1: 4-conntected aobtc ligand)

Topology for Sc1

The links to Atom Sc1

Ti1	0.0000	0.5000	0.5000	(0 0 0)	5.154A	1
Ti1	1.0000	0.5000	0.5000	(1 0 0)	7.024A	1
Ti1	0.0000	0.5000	-0.5000	(0 0 -1)	8.453A	1
Ti1	0.0000	-0.5000	-0.5000	(0 -1 -1)	10.644A	1

Topology for Ti1

The links to Atom Ti1

Sc1	-0.3128	0.4661	0.7865	(0 1 1)	5.154A	1
Sc1	0.3128	0.5339	0.2135	(0 0 0)	5.154A	1
Sc1	0.6872	0.4661	0.7865	(1 1 1)	7.024A	1
Sc1	-0.6872	0.5339	0.2135	(-1 0 0)	7.024A	1
Sc1	-0.3128	0.4661	-0.2135	(0 1 0)	8.453A	1
Sc1	0.3128	0.5339	1.2135	(0 0 1)	8.453A	1
Sc1	-0.3128	-0.5339	-0.2135	(0 0 0)	10.644A	1
Sc1	0.3128	1.5339	1.2135	(0 1 1)	10.644A	1

Coordination sequences

Sc1:	1	2	3	4	5	6	7	8	9	10
Num	4	22	24	82	64	182	124	322	204	502
Cum	5	27	51	133	197	379	503	825	1029	1531

Ti1:	1	2	3	4	5	6	7	8	9	10
Num	8	12	48	42	128	92	248	162	408	252

Cum	9	21	69	111	239	331	579	741	1149	1401

Vertex symbols for selected sublattice

Sc1 Point (Schlafli) symbol:$\{4^6\}$

Extended point symbol:[4.4.4.4.4.4]

Ti1 Point (Schlafli) symbol:$\{4^{12}.6^{12}.8^4\}$

Extended point symbol:[4.4.4.4.4.4.4.4.4.4.4.4.6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).

6(4).6(4).6(4).6(4).8(24).8(24).8(24).8(24)]

Point (Schlafli) symbol for net: $\{4^{12}.6^{12}.8^4\}\{4^6\}_2$

4,8-*c* net with stoichiometry (4-*c*)$_2$(8-*c*); 2-nodal net

Topological type: flu/fluorite; sqc169 (topos&RCSR.ttd) $\{4^{12}.6^{12}.8^4\}\{4^6\}_2$ - VS [4.4.

4.4.4.4][4.4.4.4.4.4.4.4.4.4.4.4.6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6

(2).*.*.*.*]