Electronic Supporting Information (ESI)

A Series of Cobalt and Nickel Clusters Based on Thiol-containing Ligands Accompanied by *in situ* Ligand Formation

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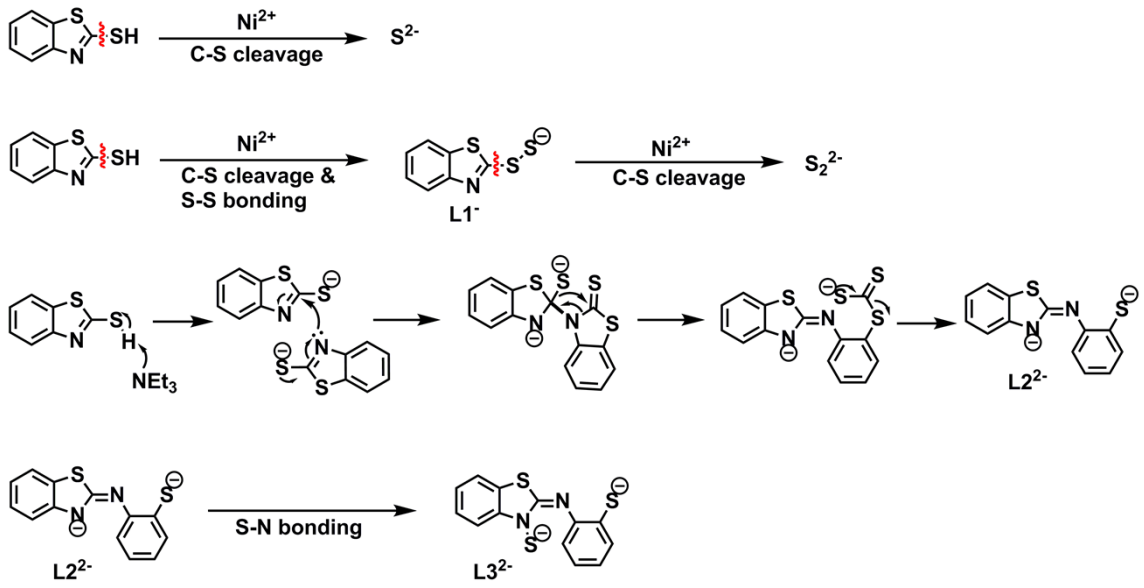

Scheme. S1 The possible formation routes of the *in situ* generated ligands from HMBT.

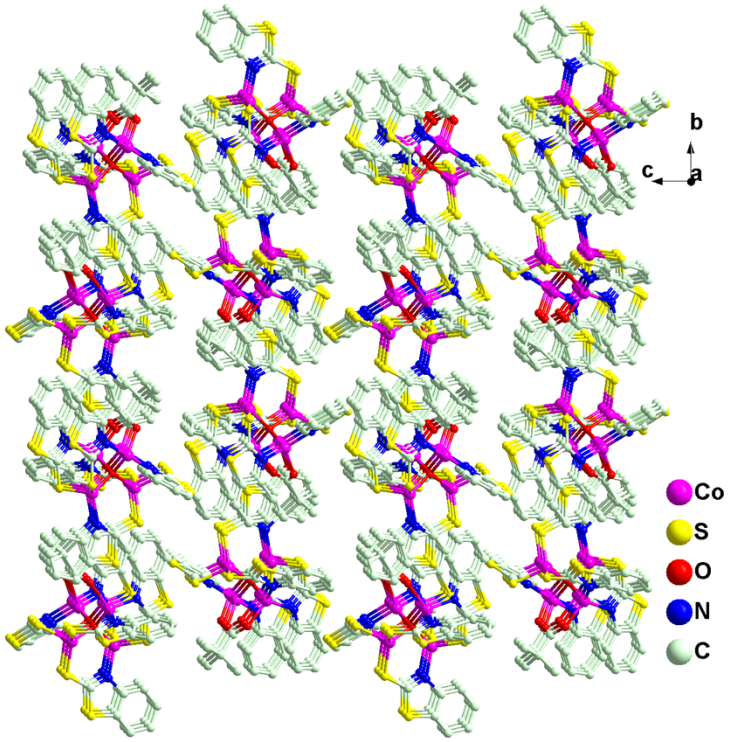

Fig. S1 The supramolecular packing mode of **1**.

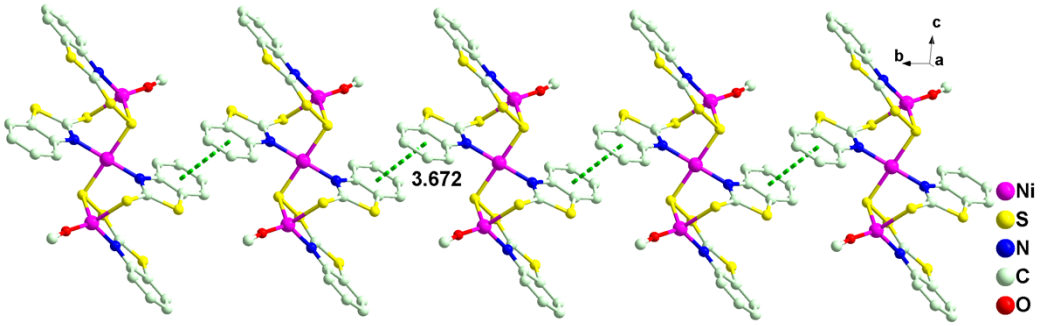

Fig. S2 The 1D supramolecular chain of **2**.

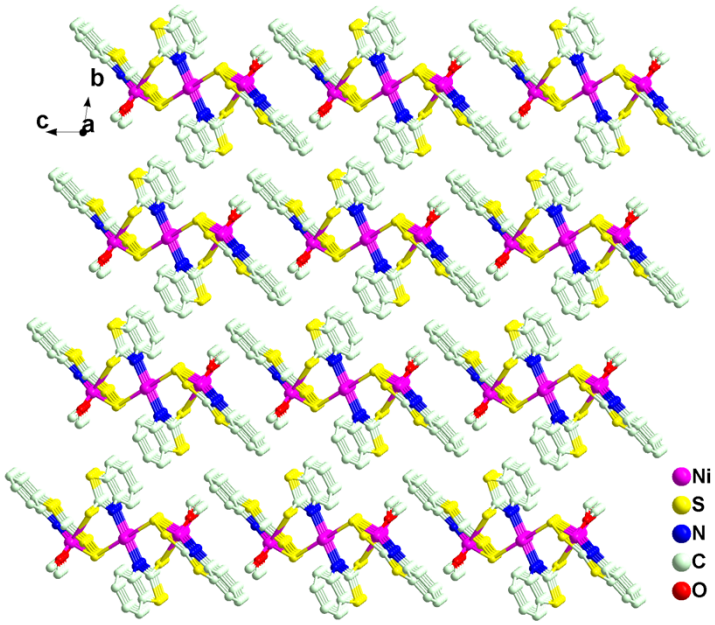

Fig. S3 The supramolecular packing mode of **2**.

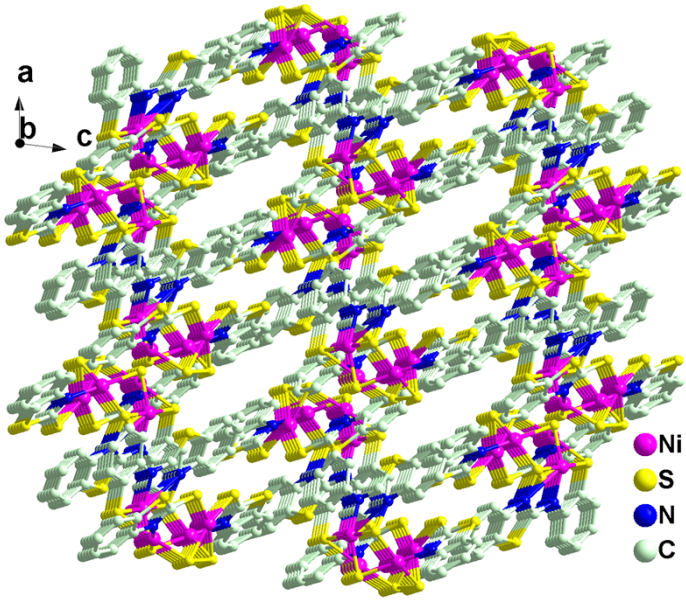

Fig. S4 The supramolecular packing mode of **3**.

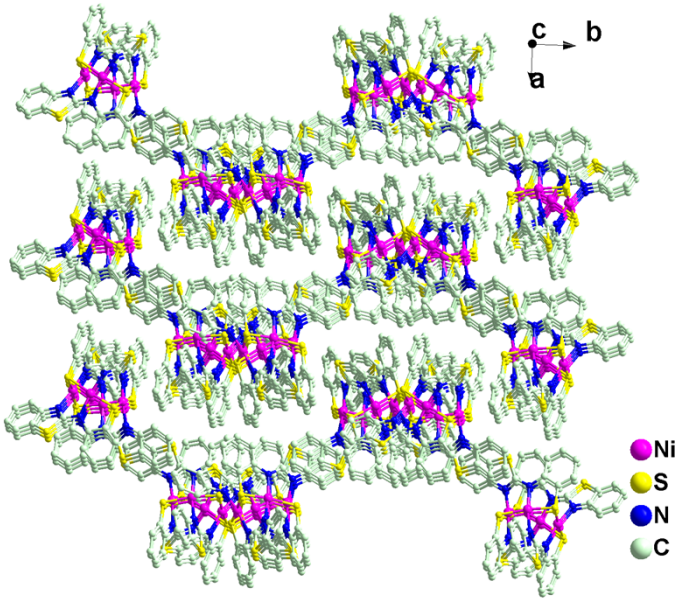

Fig. S5 The supramolecular packing mode of **4**.

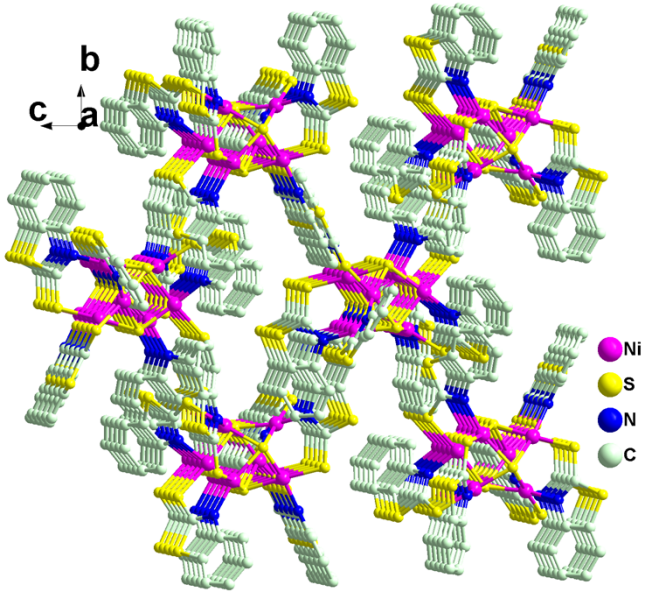

Fig. S6 The supramolecular packing mode of **5**.

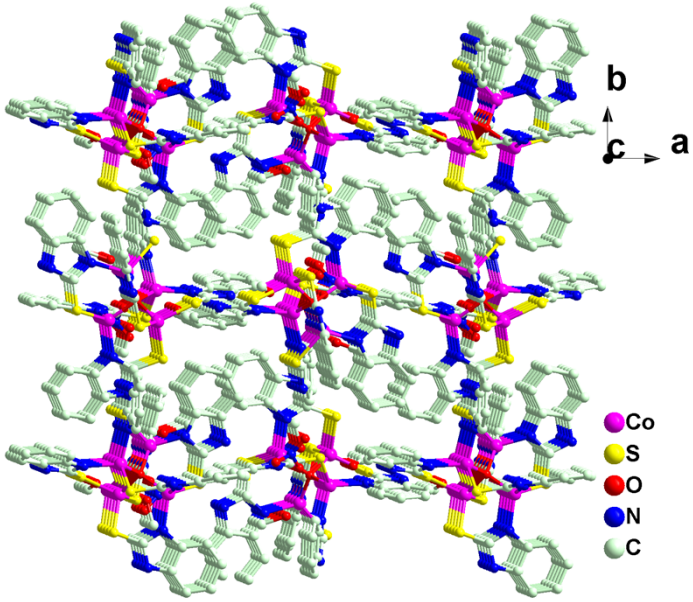

Fig. S7 The supramolecular packing mode of **6**.

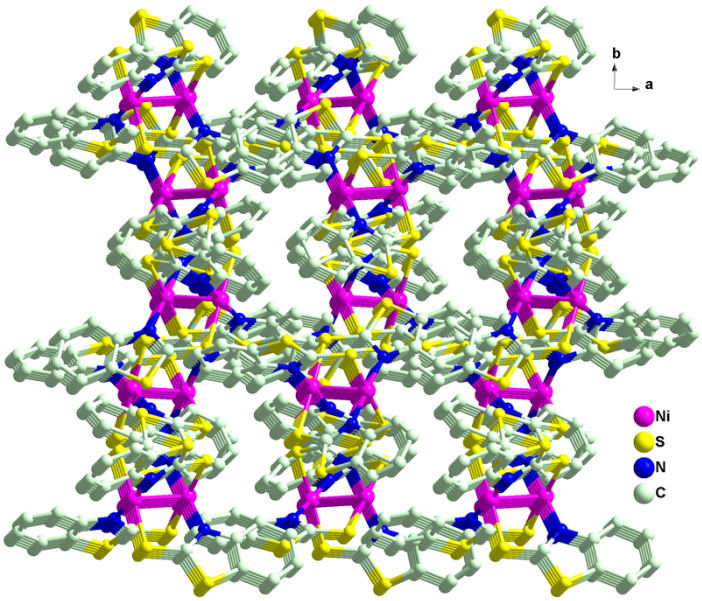

Fig. S8 The supramolecular packing mode of **7**.

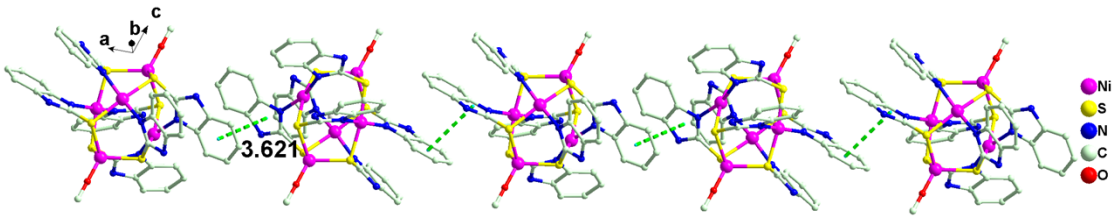

Fig. S9 The 1D supramolecular chain of **8**.

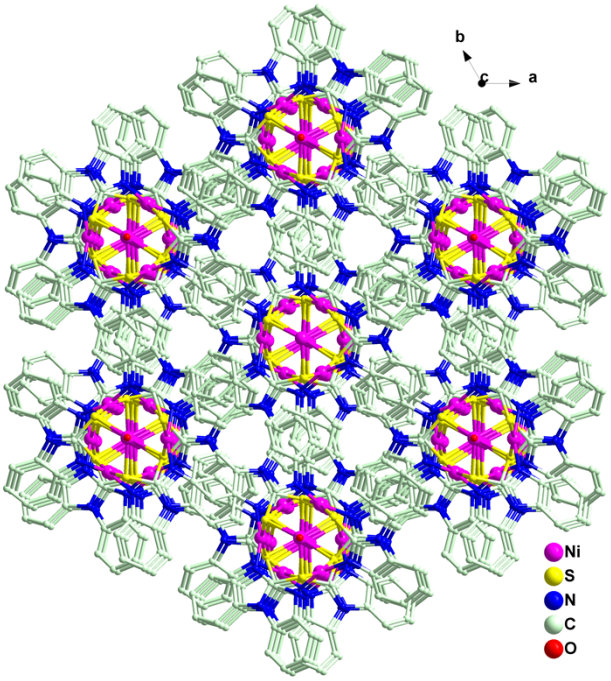

Fig. S10 The supramolecular packing mode of **8**.

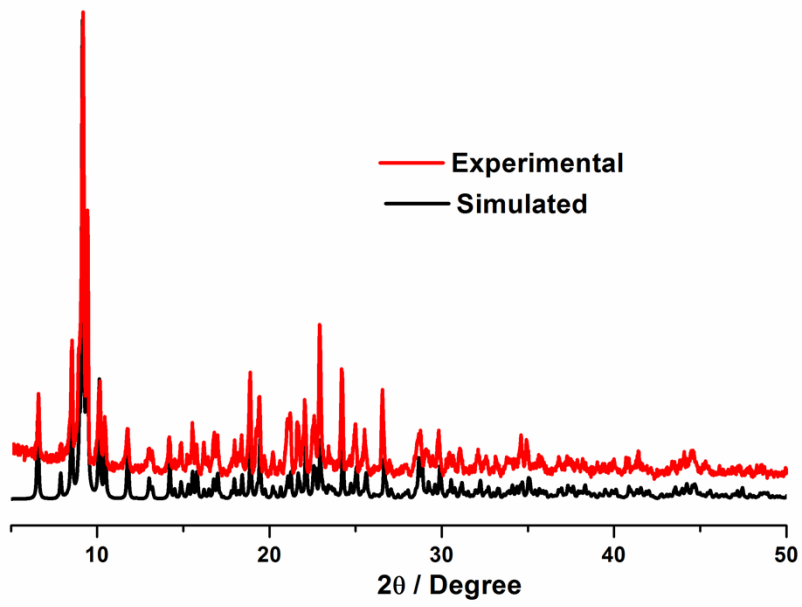

Fig. S11 The simulated and experimental PXRD patterns of **1**.

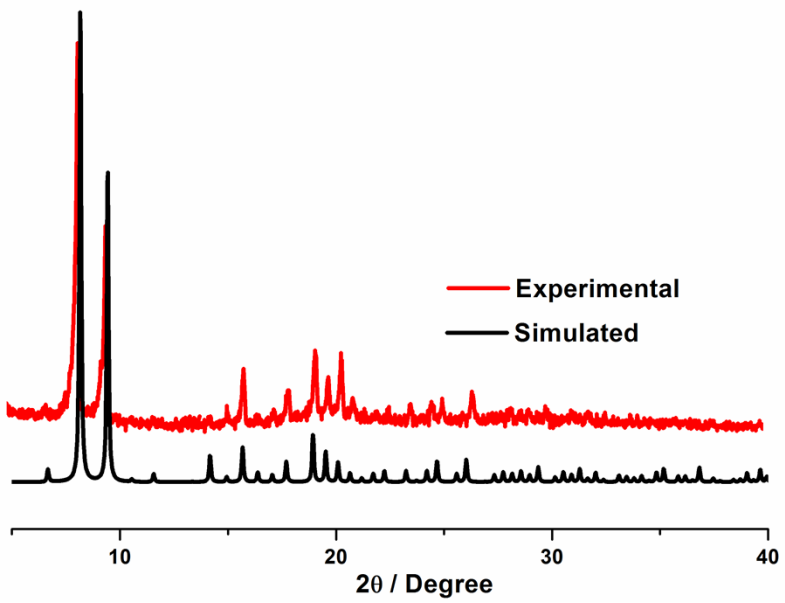

Fig. S12 The simulated and experimental PXRD patterns of **6**.

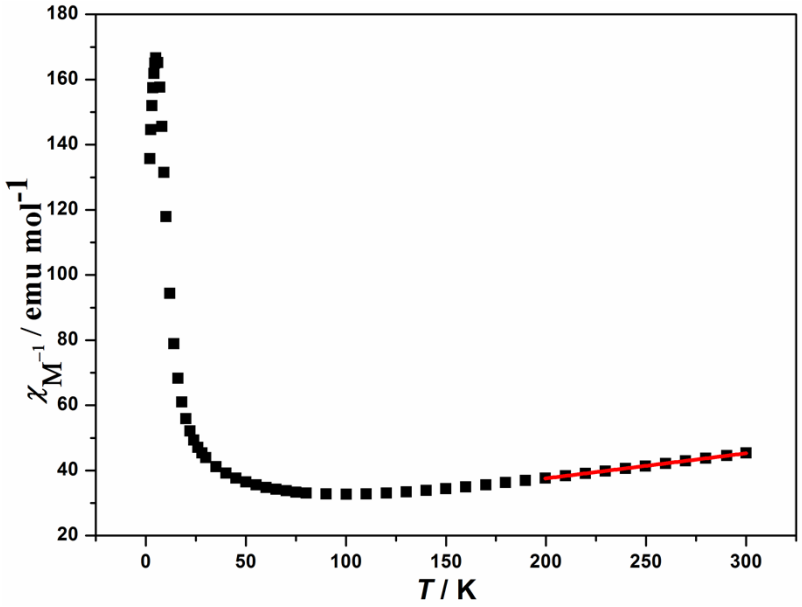

Fig. S13 The χ_M^{-1} *vs T* plot of **1**. Solid lines represent the Curie-Weiss fitting.

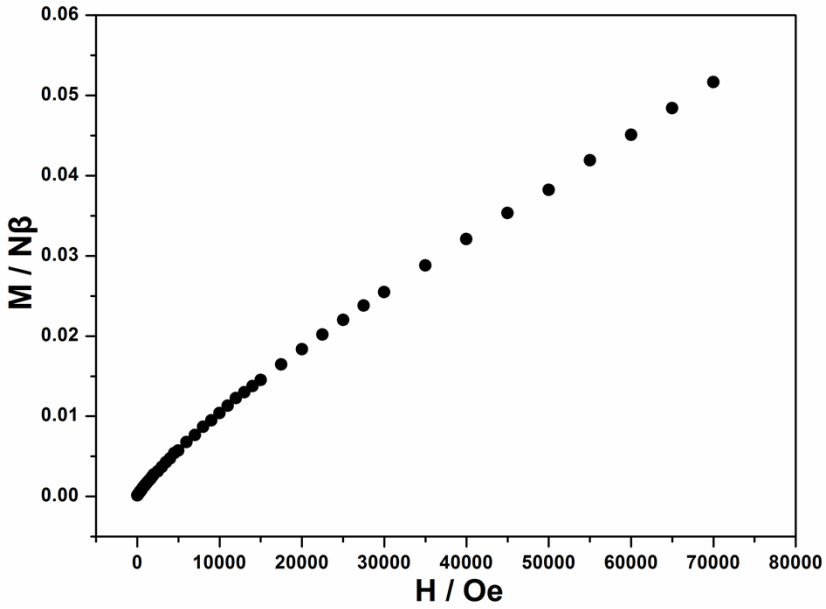

Fig. S14 The plot of *M vs H* for **1**.

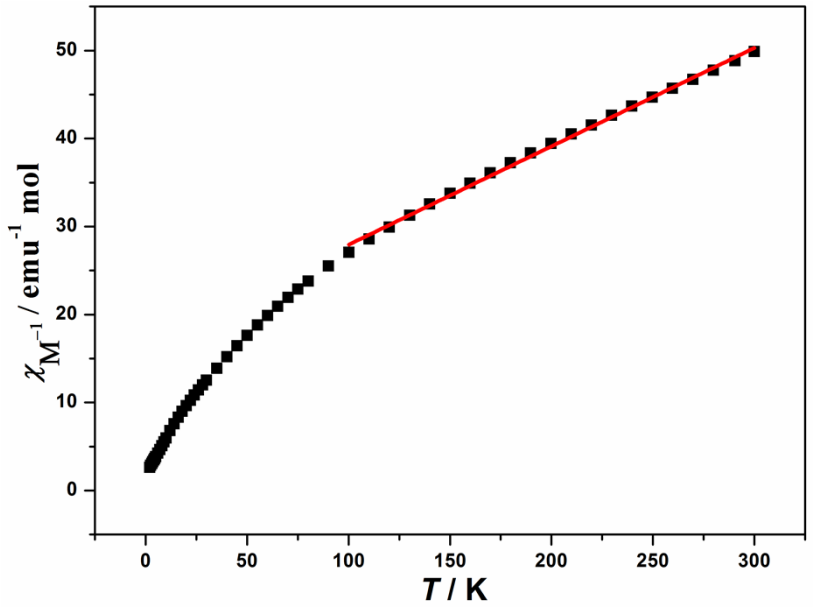

Fig. S15 The χ_M^{-1} *vs T* plot of **6**. Solid lines represent the Curie-Weiss fitting.

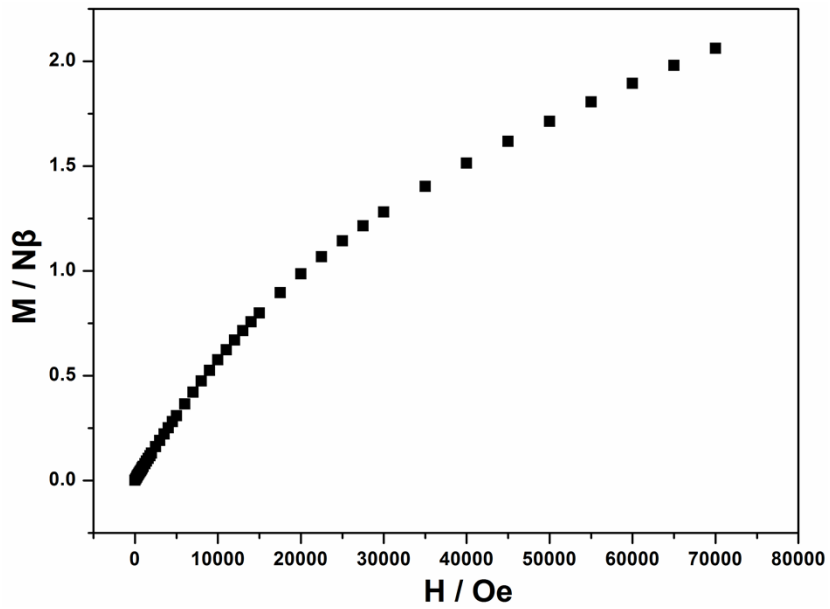

Fig. S16 The plot of *M vs H* for **6**.

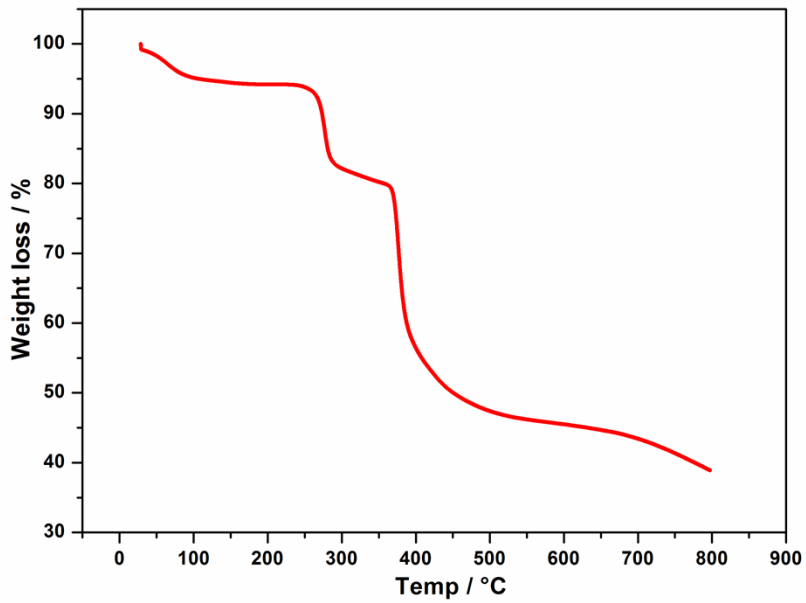

Fig. S17 The TG curve of **6**.

As shown in Fig. S17, complex **6** showed a gradual weight loss of 5.76% between ambient temperature and 180°C in agreement with the theoretical value of removing one lattice water molecule and two lattice methanol molecules (theoretically Calcd. 6.11% for **6**). A plateau was present between 180°C and 230°C. Further heating above 250 °C causes the framework to collapse accompanied by the decomposition of the organic ligands.

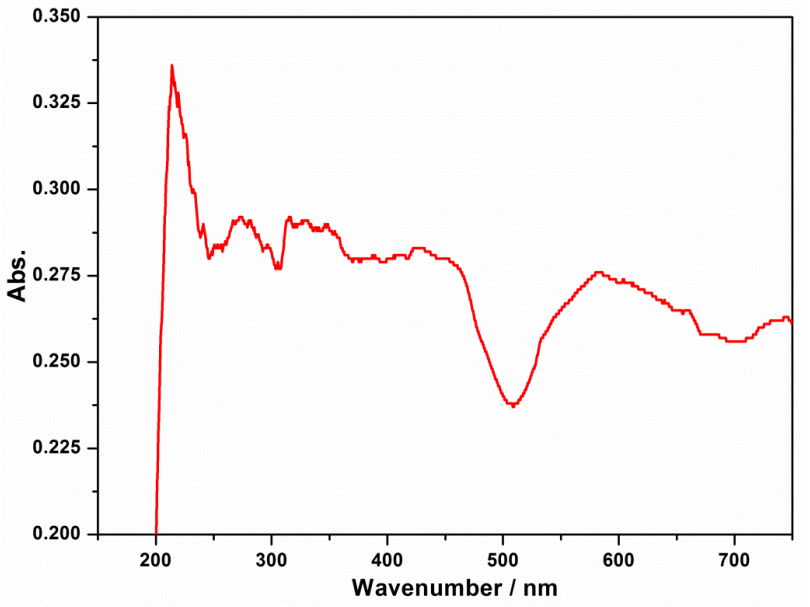

Fig. S18 The solid UV-VIS spectra of **1**.

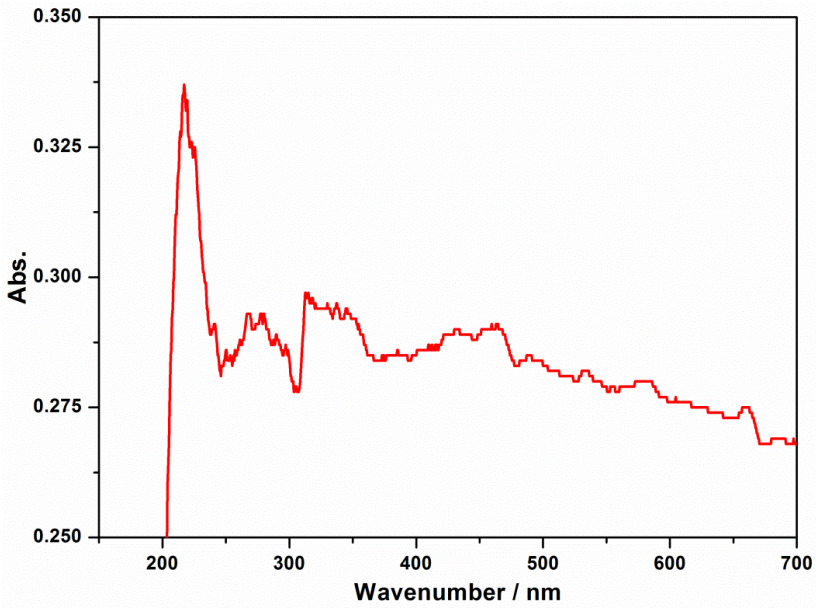

Fig. S19 The solid UV-VIS spectra of **2**.

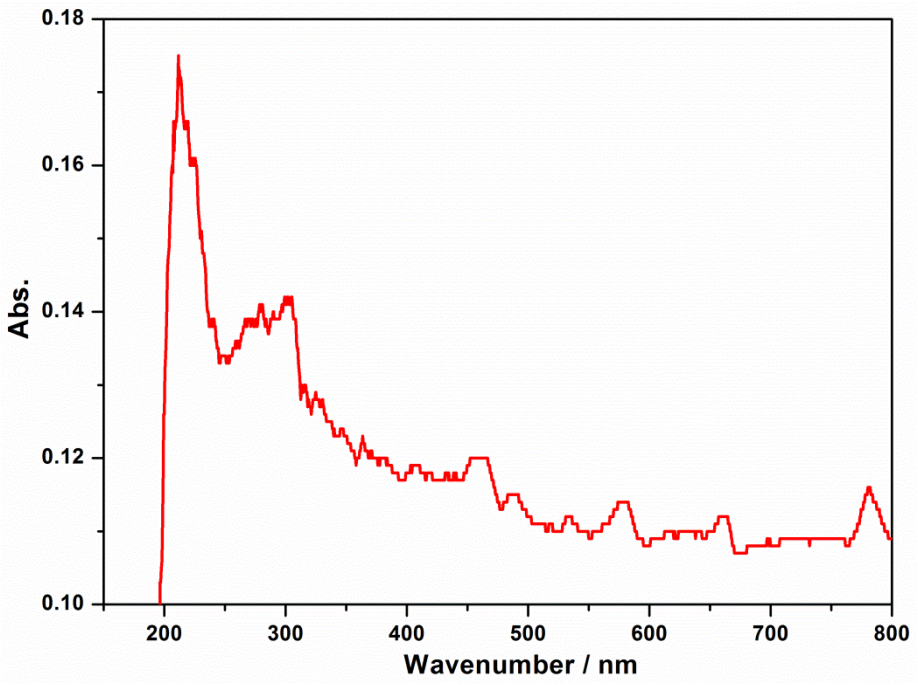

Fig. S20 The solid UV-VIS spectra of **3**.

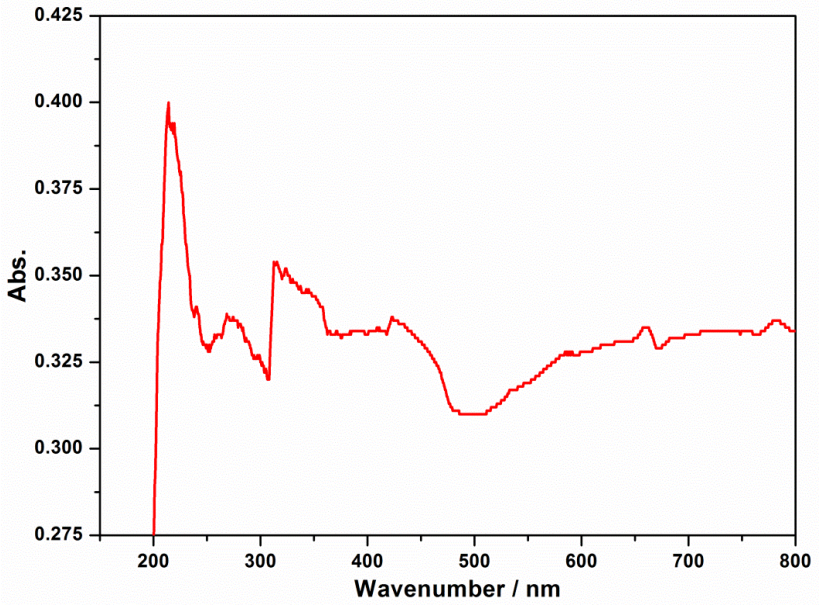

Fig. S21 The solid UV-VIS spectra of **4**.

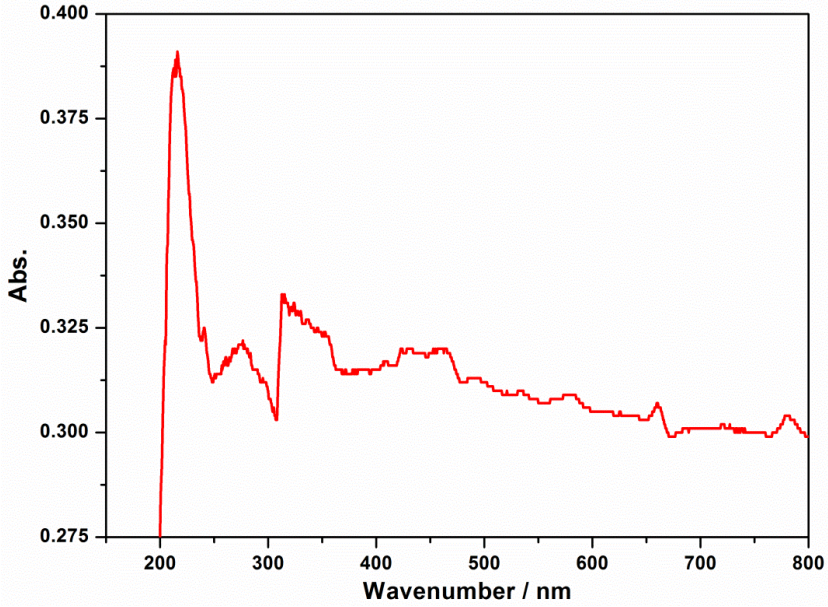

Fig. S22 The solid UV-VIS spectra of **5**.

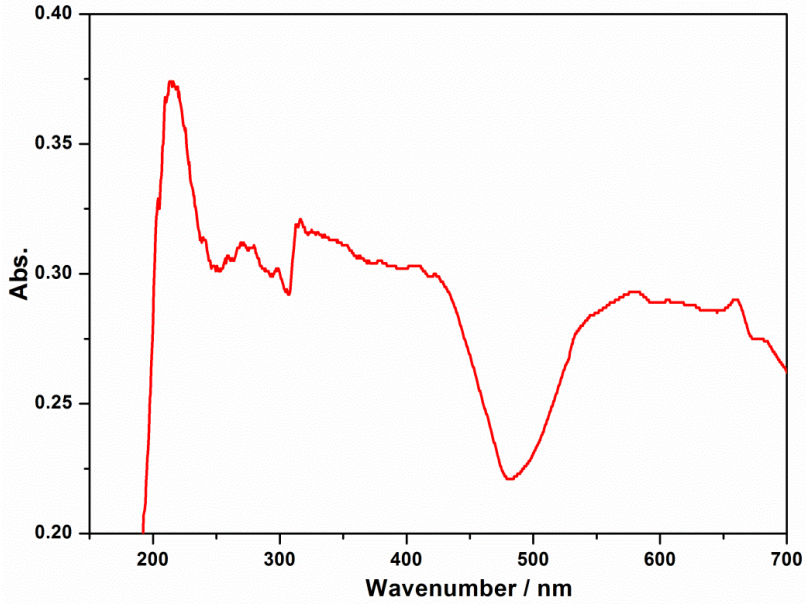

Fig. S23 The solid UV-VIS spectra of **6**.

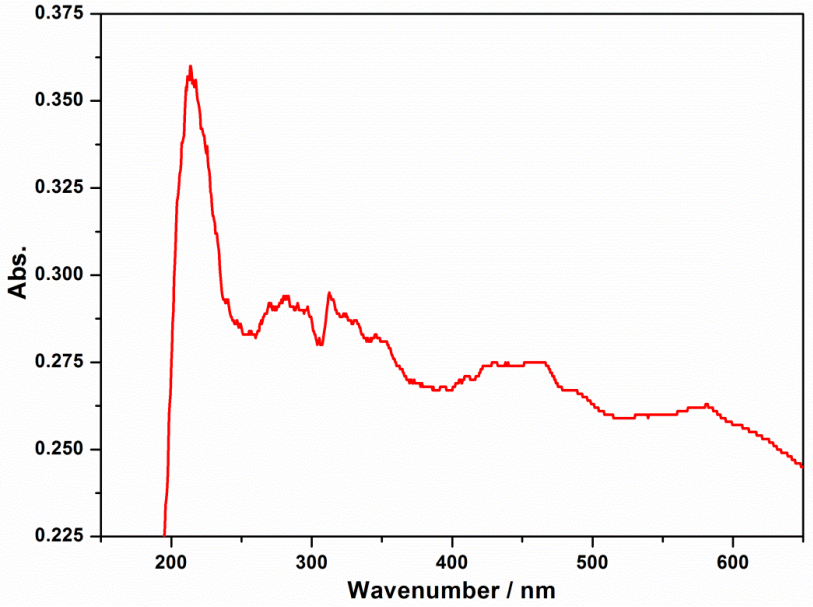

Fig. S24 The solid UV-VIS spectra of **7**.

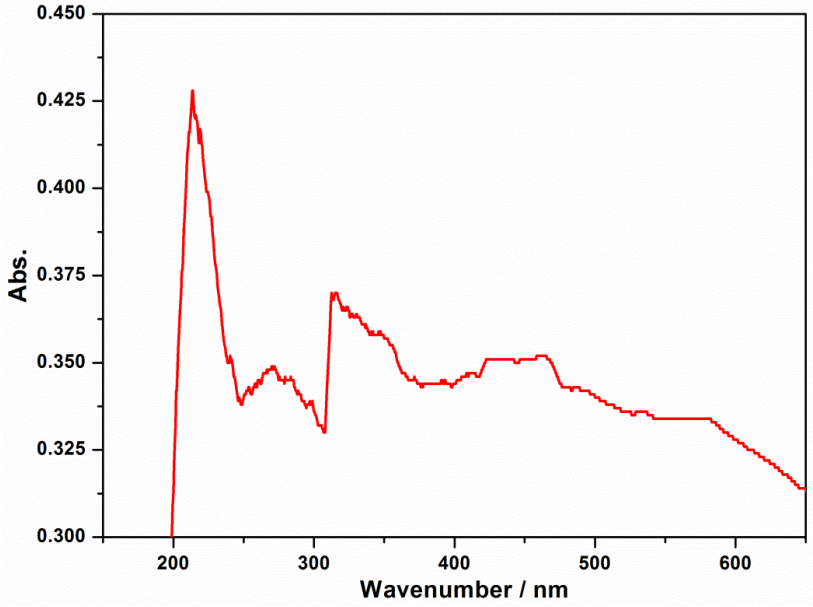

Fig. S25 The solid UV-VIS spectra of **8**.

Table S1 Bond valences (s) calculated as $s = \exp[(r_0-r)/B]$ with B = 0.37, r_0 = 2.02 for Co(III)-S pairs, r_0 = 1.75 for Co(III)–N pairs and r_0 = 1.637 for Co(III)–O pairs.[1-3]

Co1:

Nr	Bond	Dist	r_0	B	Sum	Diff
1	Co1-O1	1.9530	1.637	0.37	1.78	1.22
2	Co1-N1	2.025	1.75	0.37		
3	Co1-N3	2.031	1.75	0.37		
4	Co1-S3	2.3507	2.02	0.37		

Co2:

Nr	Bond	Dist	r_0	B	Sum	Diff
1	Co2-O1	1.962	1.637	0.37	1.79	1.21
2	Co2-S4	2.3092	2.02	0.37		
3	Co2-S4	2.3092	2.02	0.37		
4	Co2-S4	2.3092	2.02	0.37		

Table S2 The selected bond lengths [Å] and angles [º] of **1-8**.

1			
Co(1)-O(1)	1.952(2)	Co(1)-O(2)	1.957(2)
Co(1)-N(1)	2.021(2)	Co(1)-N(3)	2.037(2)
Co(4)-O(1)	1.9262(19)	Co(4)-N(5)	2.012(2)
Co(4)-S(8)	2.2933(12)	Co(4)-S(6)	2.2935(11)
Co(3)-O(1)	1.9342(19)	Co(3)-S(10)	2.2804(11)
Co(3)-S(3)	2.3007(11)	Co(3)-S(1)	2.3104(12)
Co(2)-O(1)	1.951(2)	Co(2)-O(3)	1.966(2)
Co(2)-N(2)	2.021(3)	Co(2)-N(4)	2.028(3)
O(1)-Co(1)-O(2)	106.71(9)	O(1)-Co(1)-N(1)	108.99(9)
O(2)-Co(1)-N(1)	111.14(10)	O(1)-Co(1)-N(3)	110.50(9)
O(2)-Co(1)-N(3)	103.26(10)	N(1)-Co(1)-N(3)	115.81(10)
O(1)-Co(4)-S(8)	104.90(7)	O(1)-Co(4)-N(5)	118.73(9)
N(5)-Co(4)-S(8)	105.19(8)	O(1)-Co(4)-S(6)	108.82(6)

N(5)-Co(4)-S(6)	104.28(8)	S(8)-Co(4)-S(6)	115.37(4)
O(1)-Co(2)-O(3)	104.22(9)	O(1)-Co(2)-N(2)	116.55(9)
O(3)-Co(2)-N(2)	111.39(11)	O(1)-Co(2)-N(4)	102.68(9)
O(3)-Co(2)-N(4)	107.66(10)	N(2)-Co(2)-N(4)	113.43(10)
O(1)-Co(3)-S(10)	109.23(6)	O(1)-Co(3)-S(3)	112.25(6)
S(10)-Co(3)-S(3)	126.17(4)	O(1)-Co(3)-S(1)	109.68(7)
S(10)-Co(3)-S(1)	101.67(4)	S(3)-Co(3)-S(1)	95.20(4)
		2	
Ni(1)-N(2)#1	1.908(4)	Ni(1)-N(2)	1.908(4)
Ni(1)-S(3)	2.2452(14)	Ni(1)-S(3)#1	2.2452(14)
Ni(2)-O(1)	1.657(5)	Ni(2)-N(1)	2.014(4)
Ni(2)-S(3)	2.3356(17)	Ni(2)-S(5)	2.3484(17)
N(2)#1-Ni(1)-N(2)	180.00(12)	N(2)#1-Ni(1)-S(3)	87.18(11)
N(2)-Ni(1)-S(3)	92.82(11)	N(2)#1-Ni(1)-S(3)#1	92.82(11)
N(2)-Ni(1)-S(3)#1	87.18(11)	S(3)-Ni(1)-S(3)#1	180.00(6)
O(1)-Ni(2)-N(1)	130.40(19)	O(1)-Ni(2)-S(3)	117.48(17)
N(1)-Ni(2)-S(3)	89.87(12)	O(1)-Ni(2)-S(5)	113.73(16)
N(1)-Ni(2)-S(5)	96.32(12)	S(3)-Ni(2)-S(5)	104.02(6)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1.			
		3	
Ni(1)-N(4)	1.900(9)	Ni(1)-S(4)	2.130(3)
Ni(1)-S(3)	2.144(3)	Ni(1)-S(2)	2.150(3)
Ni(2)-N(1)	1.935(10)	Ni(2)-S(5)	2.170(3)
Ni(2)-S(4)	2.188(3)	Ni(2)-S(2)	2.262(3)
Ni(4)-S(5)	2.179(3)	Ni(4)-S(10)	2.183(4)
Ni(4)-S(8)	2.196(4)	Ni(4)-S(6)	2.200(4)
Ni(3)-N(2)	1.944(10)	Ni(3)-S(6)	2.162(4)
Ni(3)-S(4)	2.193(3)	Ni(3)-S(3)	2.259(3)
N(4)-Ni(1)-S(4)	151.8(3)	N(4)-Ni(1)-S(3)	91.2(3)
S(4)-Ni(1)-S(3)	88.78(12)	N(4)-Ni(1)-S(2)	91.0(3)
S(4)-Ni(1)-S(2)	90.58(12)	S(3)-Ni(1)-S(2)	176.52(13)
N(1)-Ni(2)-S(5)	87.8(3)	N(1)-Ni(2)-S(4)	176.3(3)
S(5)-Ni(2)-S(4)	94.16(13)	N(1)-Ni(2)-S(2)	92.3(3)
S(5)-Ni(2)-S(2)	171.18(13)	S(4)-Ni(2)-S(2)	86.21(12)
S(5)-Ni(4)-S(10)	161.61(15)	S(5)-Ni(4)-S(8)	104.73(14)
S(10)-Ni(4)-S(8)	93.66(15)	S(5)-Ni(4)-S(6)	56.39(12)
S(10)-Ni(4)-S(6)	105.25(14)	S(8)-Ni(4)-S(6)	160.98(14)
N(2)-Ni(3)-S(6)	89.6(3)	N(2)-Ni(3)-S(4)	176.0(3)
S(6)-Ni(3)-S(4)	94.36(13)	N(2)-Ni(3)-S(3)	91.6(3)
S(6)-Ni(3)-S(3)	174.99(14)	S(4)-Ni(3)-S(3)	84.35(12)
		4	
Ni(1)-N(3)	1.898(5)	Ni(1)-N(5)	1.926(5)
Ni(1)-S(5)	2.1465(18)	Ni(1)-S(7)	2.2483(18)

Ni(4)-N(1)	1.882(5)	Ni(4)-N(8)	1.936(5)
Ni(4)-S(7)	2.1487(19)	Ni(4)-S(8)	2.2795(19)
Ni(2)-N(2)	1.866(5)	Ni(2)-N(6)	1.908(5)
Ni(2)-S(6)	2.139(2)	Ni(2)-S(5)	2.265(2)
Ni(3)-N(4)	1.874(5)	Ni(3)-N(7)	1.927(5)
Ni(3)-S(8)	2.1330(18)	Ni(3)-S(6)	2.2733(18)
N(3)-Ni(1)-N(5)	169.3(2)	N(3)-Ni(1)-S(5)	82.36(15)
N(5)-Ni(1)-S(5)	88.16(16)	N(3)-Ni(1)-S(7)	92.66(15)
N(5)-Ni(1)-S(7)	96.95(16)	S(5)-Ni(1)-S(7)	174.68(7)
N(1)-Ni(4)-N(8)	169.9(2)	N(1)-Ni(4)-S(7)	82.72(16)
N(8)-Ni(4)-S(7)	88.35(16)	N(1)-Ni(4)-S(8)	91.04(16)
N(8)-Ni(4)-S(8)	97.77(16)	S(7)-Ni(4)-S(8)	173.65(7)
N(2)-Ni(2)-N(6)	170.0(2)	N(2)-Ni(2)-S(6)	82.90(16)
N(6)-Ni(2)-S(6)	88.73(17)	N(2)-Ni(2)-S(5)	92.03(16)
N(6)-Ni(2)-S(5)	96.11(17)	S(6)-Ni(2)-S(5)	174.50(8)
N(4)-Ni(3)-N(7)	169.5(2)	N(4)-Ni(3)-S(8)	82.43(15)
N(7)-Ni(3)-S(8)	88.93(15)	N(4)-Ni(3)-S(6)	90.41(15)
N(7)-Ni(3)-S(6)	98.23(15)	S(8)-Ni(3)-S(6)	172.83(7)
		5	
Ni(4)-N(4)	1.961(3)	Ni(4)-S(14)	2.1945(11)
Ni(4)-S(15)	2.2226(13)	Ni(4)-S(12)	2.2260(15)
Ni(3)-N(3)	1.987(3)	Ni(3)-S(15)	2.2188(12)
Ni(3)-S(14)	2.2326(12)	Ni(3)-S(8)	2.2404(14)
Ni(1)-N(1)	1.969(4)	Ni(1)-S(15)	2.1849(13)
Ni(1)-S(13)	2.2148(12)	Ni(1)-S(9)	2.2298(14)
Ni(2)-N(2)	1.967(4)	Ni(2)-S(13)	2.2092(13)
Ni(2)-S(14)	2.2214(13)	Ni(2)-S(7)	2.2326(15)
Ni(5)-N(5)	1.970(4)	Ni(5)-S(15)	2.1998(12)
Ni(5)-S(13)	2.2490(12)	Ni(5)-S(10)	2.2581(14)
Ni(6)-N(6)	1.972(4)	Ni(6)-S(13)	2.1961(13)
Ni(6)-S(14)	2.2341(12)	Ni(6)-S(11)	2.2360(14)
N(4)-Ni(4)-S(14)	166.16(11)	N(4)-Ni(4)-S(15)	86.35(11)
S(14)-Ni(4)-S(15)	92.07(5)	N(4)-Ni(4)-S(12)	87.76(12)
S(14)-Ni(4)-S(12)	94.64(5)	S(15)-Ni(4)-S(12)	172.78(5)
N(3)-Ni(3)-S(15)	86.21(11)	N(3)-Ni(3)-S(14)	168.90(12)
S(15)-Ni(3)-S(14)	91.16(5)	N(3)-Ni(3)-S(8)	89.58(11)
S(15)-Ni(3)-S(8)	175.04(6)	S(14)-Ni(3)-S(8)	93.47(5)
N(1)-Ni(1)-S(15)	167.56(12)	N(1)-Ni(1)-S(13)	87.04(11)
S(15)-Ni(1)-S(13)	91.22(5)	N(1)-Ni(1)-S(9)	87.57(12)
S(15)-Ni(1)-S(9)	95.11(6)	S(13)-Ni(1)-S(9)	172.64(6)
N(2)-Ni(2)-S(13)	167.95(11)	N(2)-Ni(2)-S(14)	86.47(11)
S(13)-Ni(2)-S(14)	90.77(5)	N(2)-Ni(2)-S(7)	89.86(11)
S(13)-Ni(2)-S(7)	92.99(6)	S(14)-Ni(2)-S(7)	176.24(5)
N(5)-Ni(5)-S(15)	165.59(12)	N(5)-Ni(5)-S(13)	86.54(11)
S(15)-Ni(5)-S(13)	89.93(4)	N(5)-Ni(5)-S(10)	90.39(11)

S(15)-Ni(5)-S(10)	94.37(5)	S(13)-Ni(5)-S(10)	173.67(5)
N(6)-Ni(6)-S(13)	172.22(11)	N(6)-Ni(6)-S(14)	90.03(11)
S(13)-Ni(6)-S(14)	90.78(5)	N(6)-Ni(6)-S(11)	89.11(11)
S(13)-Ni(6)-S(11)	89.81(6)	S(14)-Ni(6)-S(11)	177.79(6)
		6	
Co(1)-O(1)	1.9530(18)	Co(1)-N(1)	2.025(4)
Co(1)-N(3)	2.031(5)	Co(1)-S(3)	2.3507(16)
Co(2)-O(1)	1.962(5)	Co(2)-S(4)	2.3092(16)
Co(2)-S(4)#2	2.3092(16)	Co(2)-S(4)#1	2.3092(16)
O(1)-Co(1)-N(1)	114.7(2)	O(1)-Co(1)-N(3)	109.91(18)
N(1)-Co(1)-N(3)	108.9(2)	O(1)-Co(1)-S(3)	106.54(5)
N(1)-Co(1)-S(3)	105.03(15)	N(3)-Co(1)-S(3)	111.69(15)
O(1)-Co(2)-S(4)	110.07(5)	O(1)-Co(2)-S(4)#2	110.07(5)
S(4)-Co(2)-S(4)#2	108.86(5)	O(1)-Co(2)-S(4)#1	110.07(5)
S(4)-Co(2)-S(4)#1	108.86(5)	S(4)#2-Co(2)-S(4)#1	108.86(5)
Symmetry transformations used to generate equivalent atoms: #1: -y+1/2,-z+1,x+1/2; #2: z-1/2,-x+1/2,-y+1.			
		7	
Ni(1)-N(3)	1.894(3)	Ni(1)-N(5)	1.897(3)
Ni(1)-N(1)	1.898(3)	Ni(1)-N(7)	1.901(3)
Ni(2)-S(3)	2.2350(13)	Ni(2)-S(1)	2.2355(13)
Ni(2)-S(4)	2.2363(13)	Ni(2)-S(2)	2.2440(12)
N(3)-Ni(1)-N(5)	89.43(13)	N(3)-Ni(1)-N(1)	90.15(13)
N(5)-Ni(1)-N(1)	179.48(15)	N(3)-Ni(1)-N(7)	179.83(16)
N(5)-Ni(1)-N(7)	90.45(14)	N(1)-Ni(1)-N(7)	89.97(14)
S(3)-Ni(2)-S(1)	178.33(4)	S(3)-Ni(2)-S(4)	89.50(5)
S(1)-Ni(2)-S(4)	89.91(5)	S(3)-Ni(2)-S(2)	90.59(5)
S(1)-Ni(2)-S(2)	89.98(5)	S(4)-Ni(2)-S(2)	178.88(4)
		8	
Ni(1)-N(1)	1.905(4)	Ni(1)-N(1)#1	1.905(4)
Ni(1)-S(3)#1	2.2269(13)	Ni(1)-S(3)	2.2270(13)
Ni(2)-O(1)	1.629(9)	Ni(2)-S(3)	2.3113(14)
Ni(2)-S(3)#2	2.3113(14)	Ni(2)-S(3)#3	2.3113(14)
N(1)-Ni(1)-N(1)#1	162.9(2)	N(1)-Ni(1)-S(3)#1	93.51(12)
N(1)#1-Ni(1)-S(3)#1	88.24(12)	N(1)-Ni(1)-S(3)	88.24(12)
N(1)#1-Ni(1)-S(3)	93.51(12)	S(3)#1-Ni(1)-S(3)	168.27(7)
O(1)-Ni(2)-S(3)	114.69(4)	O(1)-Ni(2)-S(3)#2	114.69(4)
S(3)-Ni(2)-S(3)#2	103.79(5)	O(1)-Ni(2)-S(3)#3	114.69(4)
S(3)-Ni(2)-S(3)#3	103.79(5)	S(3)#2-Ni(2)-S(3)#3	103.79(5)
Symmetry transformations used to generate equivalent atoms: #1: -x+4/3, -x+y+2/3, -z+1/6; #2: -y+1, x-y, z; #3: -x+y+1, -x+1, z.			

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