Supplementary Information

Penta- and hexa-nuclear nickel tiara-like clusters with two different thiolate bridges

Chunhong Tan, Meiliang Jin, Hao Zhang, Shengmin Hu, Tianlu Sheng* and Xintao Wu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

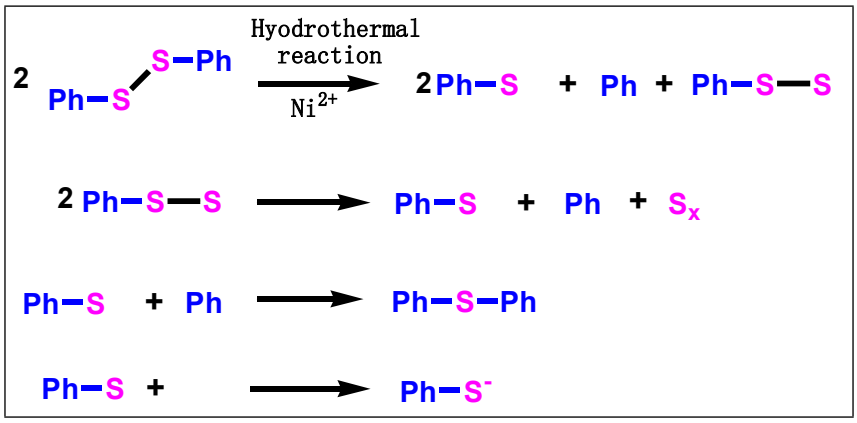
- Corresponding author:
  E-mail: *tsheng@fjirsm.ac.cn.*
  Tel: +86-591-83792294; Fax: +86-591-83719238

Supplemental synthetic procedures

cyclo-[Ni(μ-EDT)]$_5$ (1) A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (144 mg, 0.4 mmol), 1,2-ethanedithiol (0.036 ml, 0.4 mmol) and sodium ethylate (56 mg, 0.8 mmol) in 12 ml ethanol was stirred at room temperature for 1 h. Then DMF (4 ml) were added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 403 K for 16 h, After the autoclave was cooled to room temperature, black cuboid crystals of **1** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 35% for **1**).

cyclo-{[Ni(μ-S*i*Pe)$_2$]$_6$} (2) A mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (144 mg, 0.4 mmol), isopentylthiol (0.10 ml, 0.8 mmol) and sodium ethylate (56 mg, 0.8 mmol) in 12 ml ethanol was stirred at room temperature for 1 h. Then DMF (4 ml) were added. The resulting black red slurry was sealed in a 20 ml Teflonlined autoclave and heated at 403 K for 16 h, After the autoclave was cooled to room temperature, black block crystals of **2** were separated by filtration, washed with ethanol, and dried in air (yield: ca. 41% for **2** based on $Ni(ClO_4)_2 \cdot 6H_2O$).

Scheme S1. Mechanism of the in situ synthesis of thiophenol.



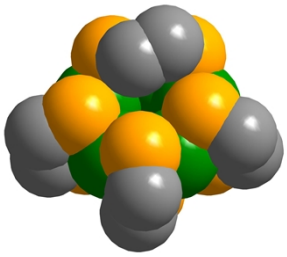


Fig. S1 Molecular view of **1** in space filling model. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

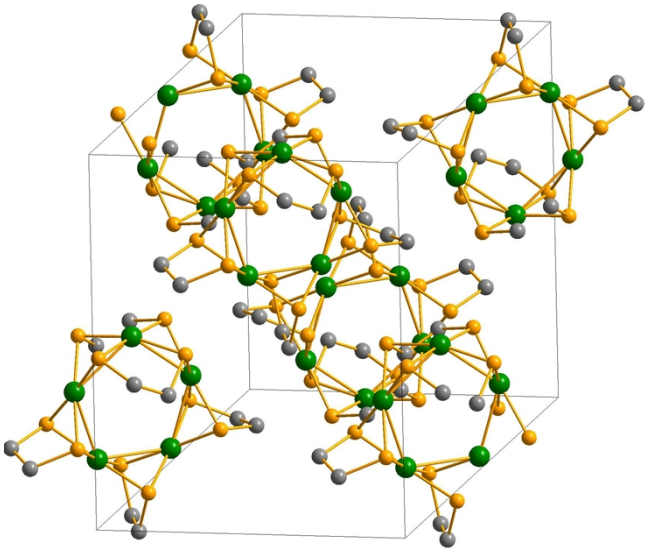


Fig. S2 Crystal packing pattern of **1**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

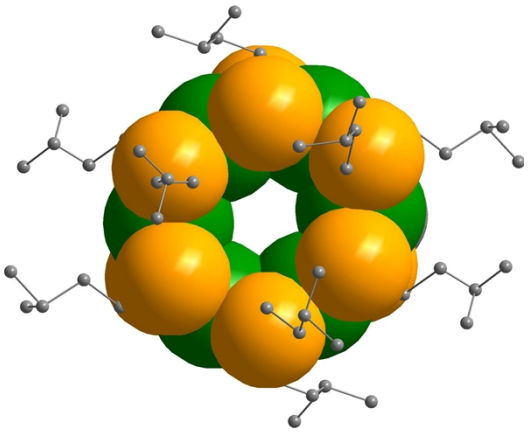


Fig. S3 Molecular view of **2** in space filling model. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

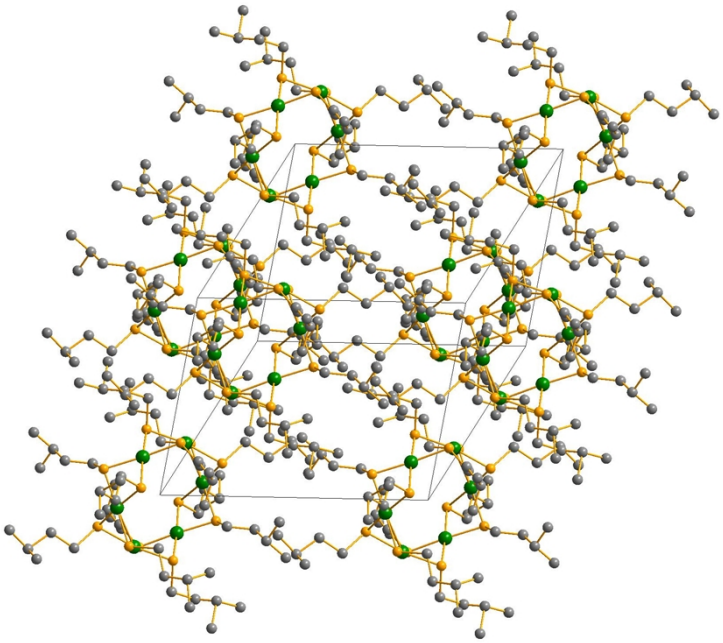


Fig. S4 Crystal packing pattern of **2**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

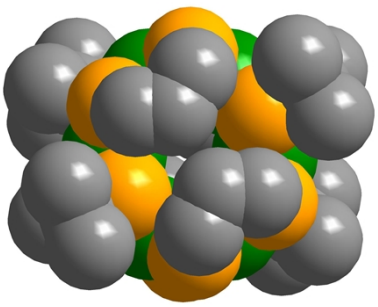


Fig. S5 Molecular view of **4** in space filling model. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

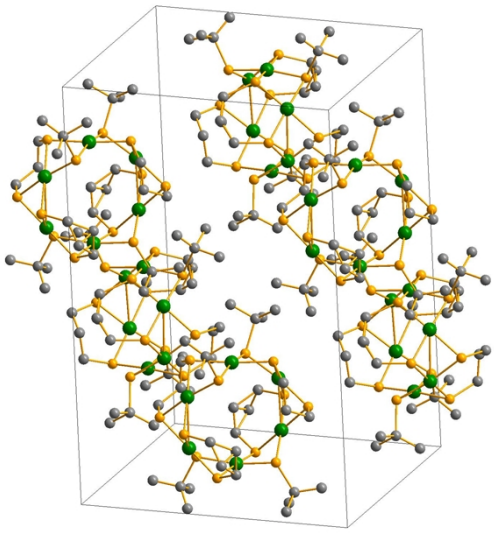


Fig. S6 Crystal packing pattern of **4**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

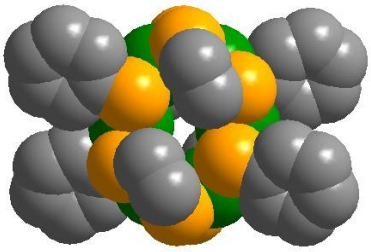


Fig. S7 Molecular view of **5** in space filling model. The hydrogen atoms and the distored carbon are omitted for clarity (Ni green, S yellow, C gray).

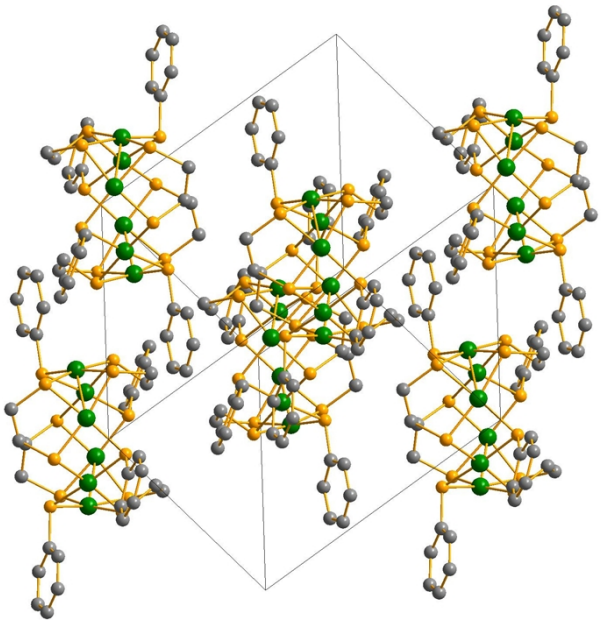


Fig. S8 Crystal packing pattern of **5**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

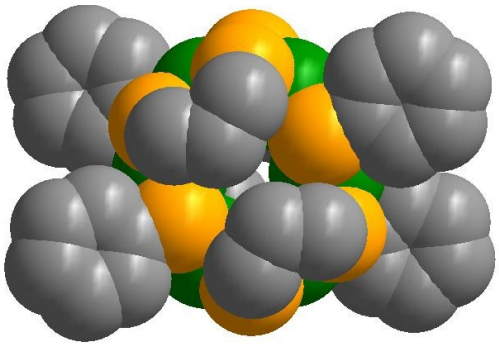


Fig. S9 Molecular view of **6** in space filling model. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

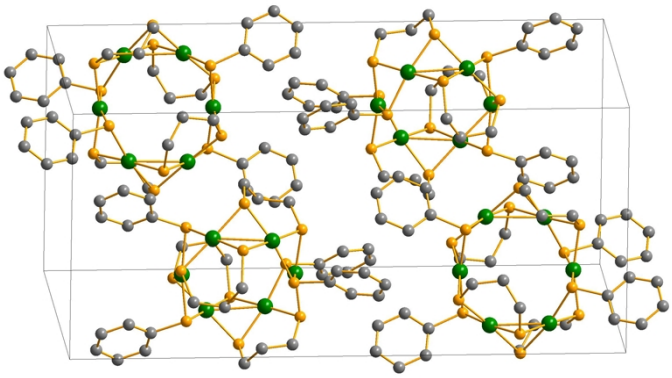


Fig. S10 Crystal packing pattern of **6**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

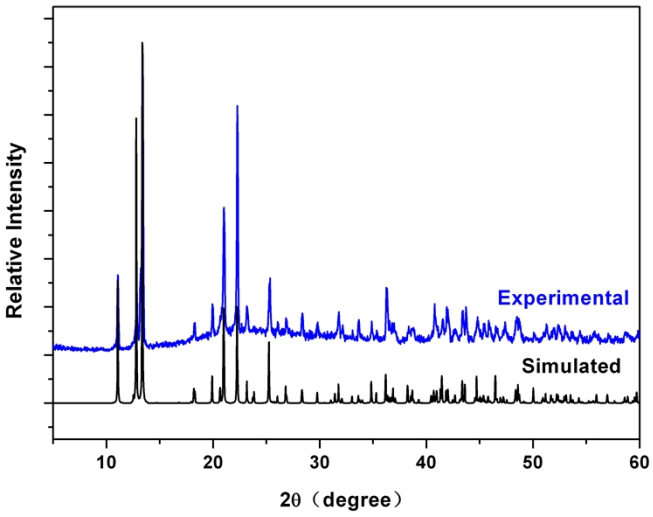


Fig. S11 Powder X-ray diffractions for simulated and experimental **1**.

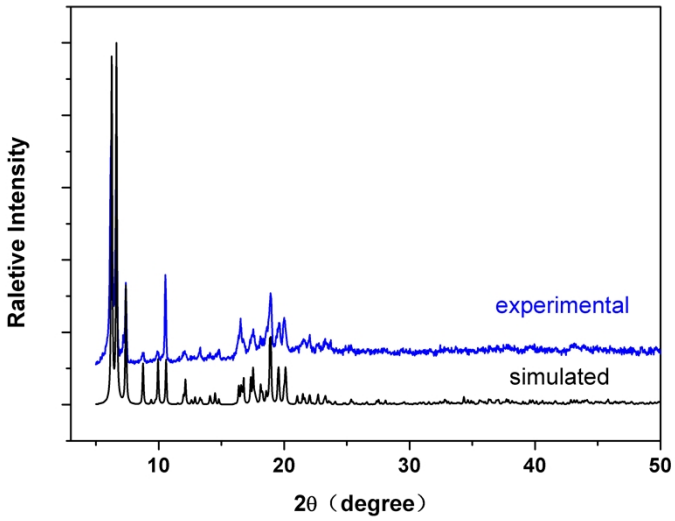


Fig. S12 Powder X-ray diffractions for simulated and experimental **2**.

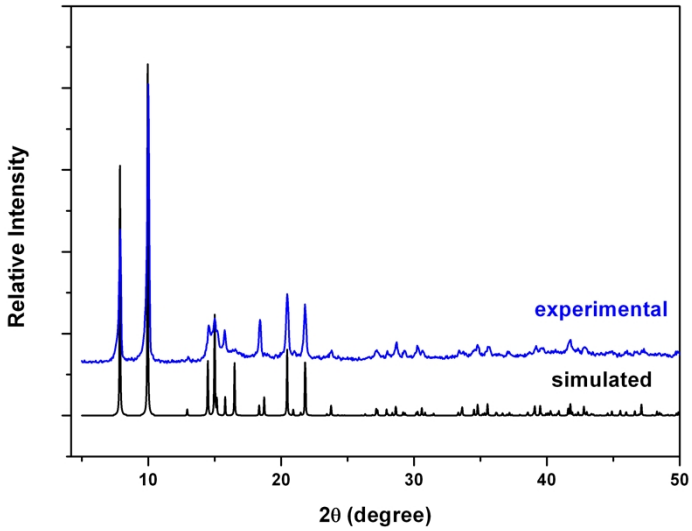


Fig. S13 Powder X-ray diffractions for simulated and experimental **3**.

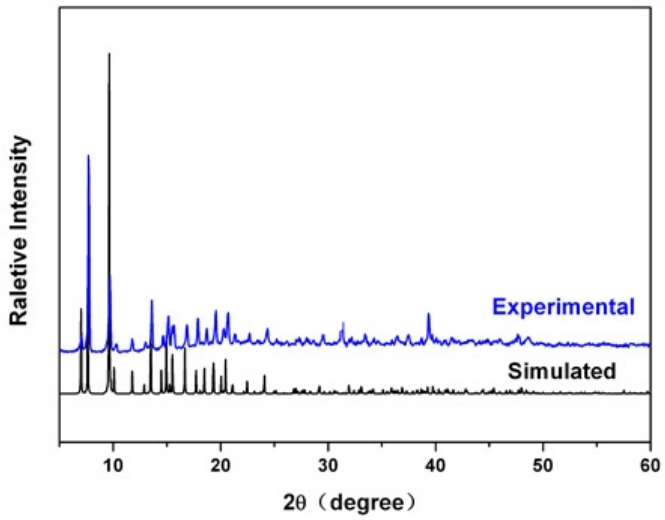


Fig. S14 Powder X-ray diffractions for simulated and experimental **4**.

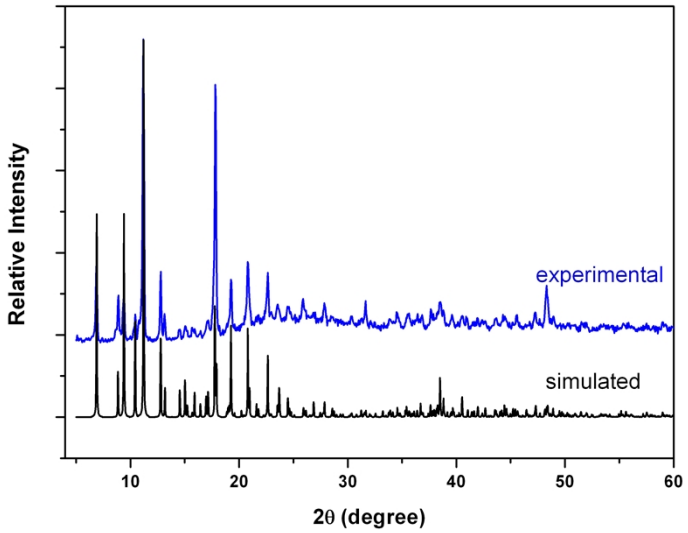


Fig. S15 Powder X-ray diffractions for simulated and experimental **5**.

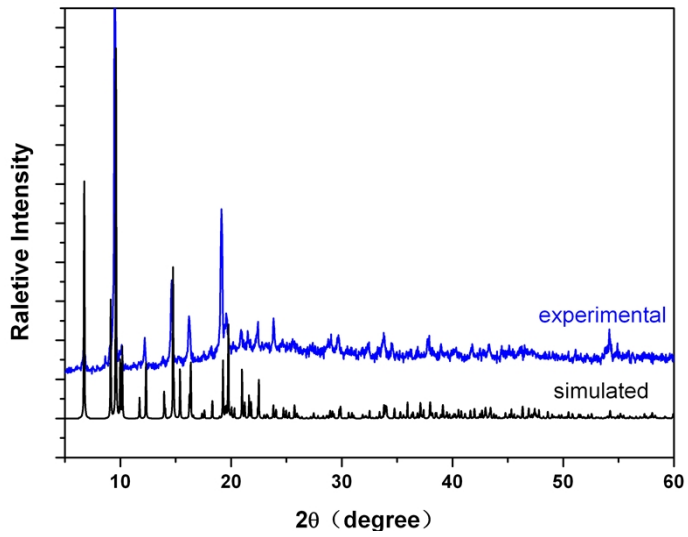


Fig. S16 Powder X-ray diffractions for simulated and experimental **6**.

Table S1 the crystal data and structure refinements for culster **1**.

Compound	**1**
Empirical formula	$C_{10}H_{20}Ni_5S_{10}$
Formula weight（g/mol）	754.41
Crystal system	Monoclinic
Space group	*C*2/*c*
Crystal appearance	black needle
Crystal Size (mm)	0.25×0.10×0.06
a (Å)	10.906(3)
b (Å)	14.095(3)
c (Å)	14.294(3)
α (°)	90
β (°)	105.160(12)
γ (°)	90
V (Å^3)	2120.9(9)
Z	4
D_c (Mg/m^3)	2.363
μ (mm^{-1})	5.337
F(000)	1520
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range (°)	2.41 -27.51
h, *k* and *l* ranges	-12≤*h*≤14
	-18≤*k*≤17
	-18≤*l*≤17
Reflections measured	8227
Independent reflections	2439
Observed Reflection($I > 2\sigma(I)$)	1855
R_{int}	0.0574
Min./max. trans.	0.6779 and 1.0000
Goodness-of-fit on F^2	1.032
Final *R** indices ($I > 2\sigma(I)$)	*R*1 = 0.0413, *wR*2 = 0.0713
R indices (all)	*R*1 = 0.0656, *wR*2 = 0.0792
Largest diff. peak and hole	0.588 and -0.501

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$

Table S2 the crystal data and structure refinements for culster **2**.

Compound	**2**
Empirical formula	$C_{60}H_{132}Ni_6S_{12}$
Formula weight（g/mol）	1590.64
Crystal system	triclinic
Space group	*P*-1
Crystal appearance	black cuboid
Crystal Size (mm)	0.25×0.20×0.20
a (Å)	10.700(8)
b (Å)	14.844(10)
c (Å)	15.567(10)
α (°)	66.82(6)
β (°)	75.32(6)
γ (°)	72.64(6)
V (Å^3)	2143(3)
Z	1
D_c (Mg/m^3)	1.232
μ (mm^{-1})	1.613
F(000)	852
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range (°)	2.76 -25.00
h, *k* and *l* ranges	-12≤*h*≤12
	-178≤*k*≤15
	-18≤*l*≤18
Reflections measured	13364
Independent reflections	7359
Observed Reflection($I > 2\sigma(I)$)	3464
R_{int}	0.0580
Min./max. trans.	0.6302 and 1.0000
Goodness-of-fit on F^2	1.048
Final *R** indices ($I > 2\sigma(I)$)	*R*1 = 0.0821, *wR*2 = 0.1361
R indices (all)	*R*1 = 0.1673, *wR*2 = 0.1640
Largest diff. peak and hole	0.493 and -0.346

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$

Table S3 the crystal data and structure refinements for culster **4**.

Compound	**4**
Empirical formula	$C_{28}H_{60}Ni_6S_{12}$
Formula weight（g/mol）	1133.74
Crystal system	Orthorhombic
Space group	$C222_1$
Crystal appearance	black needle
Crystal Size (mm)	0.35×0.15×0.15
a (Å)	15.028(17)
b (Å)	23.16(2)
c (Å)	13.417(14)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4670(9)
Z	4
D_c (Mg/m^3)	1.612
μ (mm^{-1})	2.926
F(000)	2352
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range (°)	2.22-27.27
h, k and l ranges	$-19\leq h\leq 16$
	$-28\leq k\leq 29$
	$-17\leq l\leq 17$
Reflections measured	17500
Independent reflections	5240
Observed Reflection($I > 2\sigma(I)$)	3625
R_{int}	0.0533
Min./max. trans.	0.5712 and 1.0000
Goodness-of-fit on F^2	1.064
Final R* indices ($I > 2\sigma(I)$)	$R1 = 0.0754$, $wR2 = 0.1878$
R indices (all)	$R1 = 0.1030$, $wR2 = 0.2100$
Largest diff. peak and hole	0.881 and -0.941

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$

Table S4 the crystal data and structure refinements for culster **5**.

Compound	**5**
Empirical formula	$C_{32}H_{36}Ni_6S_{12}$
Formula weight（g/mol）	1157.59
Crystal system	Monoclinic
Space group	*P*2/*n*
Crystal appearance	black cuboid
Crystal Size (mm)	0.20×0.20×0.20
a (Å)	11.621(2)
b (Å)	12.8025(18)
c (Å)	14.234(2)
α (°)	90
β (°)	103.641(10)
γ (°)	90
V (Å^3)	2058.0(6)
Z	2
D_c (Mg/m^3)	1.868
μ (mm^{-1})	3.323
F(000)	1176
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range (°)	2.04 -27.51
h, *k* and *l* ranges	-15≤*h*≤10
	-16≤*k*≤16
	-16≤*l*≤18
Reflections measured	15849
Independent reflections	4724
Observed Reflection($I > 2\sigma(I)$)	3422
R_{int}	0.0476
Min./max. trans.	0.6777 and 1.0000
Goodness-of-fit on F^2	1.144
Final *R** indices ($I > 2\sigma(I)$)	*R*1 = 0.0547, *wR*2 = 0.1374
R indices (all)	*R*1 = 0.0816, *wR*2 = 0.1659
Largest diff. peak and hole	1.176 and -0.889

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$

Table S5 the crystal data and structure refinements for culster **6**.

Compound	**6**
Empirical formula	$C_{36}H_{44}Ni_6S_{12}$
Formula weight（g/mol）	1213.69
Crystal system	Orthorhombic
Space group	*Pccn*
Crystal appearance	Black block
Crystal Size (mm)	0.20×0.15×0.15
a (Å)	11.997(7)
b (Å)	14.360(9)
c (Å)	26.228(16)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4518(5)
Z	4
D_c (Mg/m^3)	1.784
μ (mm^{-1})	3.032
F(000)	2480
Temperature (K)	293(2)
Wavelength (Å)	0.71073
θ range (°)	2.10-27.52
h, *k* and *l* ranges	-14≤*h*≤15
	-18≤*k*≤18
	-34≤*l*≤34
Reflections measured	33264
Independent reflections	5172
Observed Reflection($I > 2\sigma(I)$)	3464
R_{int}	0.0875
Min./max. trans.	0.8877 and 1.0000
Goodness-of-fit on F^2	1.095
Final *R** indices ($I > 2\sigma(I)$)	*R*1 = 0.0697, *wR*2 = 0.1708
R indices (all)	*R*1 = 0.1122, *wR*2 = 0.1998
Largest diff. peak and hole	0.878 and -0.632

$R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$

Table S6 the selected bond lengths (Å) and angles(°) for **1**.

Bond	Dist.(Å)	Bond	Dist.(Å)
Ni(1)-S(1)	2.1567(12)	Ni(3)-S(3)	2.2066(13)
Ni(1)-S(1)#1	2.1567(12)	Ni(3)-S(5)#1	2.2107(13)
Ni(1)-S(2)	2.1629(12)	Ni(3)-S(4)	2.2169(13)
Ni(1)-S(2)#1	2.1629(12)	Ni(3)-Ni(3)#1	2.7409(13)
Ni(1)-Ni(2)	2.7903(8)	S(1)-C(1)	1.832(5)
Ni(2)-S(3)	2.2034(13)	S(1)-Ni(2)#1	2.2354(13)
Ni(2)-S(2)	2.2073(12)	S(2)-C(2)	1.828(4)
Ni(2)-S(4)	2.2068(13)	S(3)-C(3)	1.823(5)
Ni(2)-S(1)#1	2.2354(13)	S(4)-C(4)	1.838(5)
Ni(2)-Ni(3)	2.7426(9)	S(5)-C(5)	1.819(5)
Ni(3)-S(5)	2.2012(13)	S(5)-Ni(3)#1	2.2107(13)
Angle	(º)	Angle	(º)
S(1)-Ni(1)-S(1)#1	162.66(7)	S(5)-Ni(3)-S(3)	97.24(5)
S(1)-Ni(1)-S(2)	94.02(5)	S(5)-Ni(3)-S(5)#1	82.05(6)
S(1)#1-Ni(1)-S(2)	85.28(5)	S(3)-Ni(3)-S(5)#1	175.00(5)
S(1)-Ni(1)-S(2)#1	85.28(5)	S(5)-Ni(3)-S(4)	178.35(5)
S(1)#1-Ni(1)-S(2)#1	94.02(5)	S(3)-Ni(3)-S(4)	81.84(5)
S(2)-Ni(1)-S(2)#1	175.37(7)	S(5)#1-Ni(3)-S(4)	98.74(5)
S(1)-Ni(1)-Ni(2)	115.28(4)	S(5)-Ni(3)-Ni(3)#1	51.75(4)
S(1)#1-Ni(1)-Ni(2)	51.82(3)	S(3)-Ni(3)-Ni(3)#1	124.44(4)
S(2)-Ni(1)-Ni(2)	51.03(3)	S(5)#1-Ni(3)-Ni(3)#1	51.44(4)
S(1)-Ni(1)-Ni(2)#1	51.82(3)	S(5)-Ni(3)-Ni(2)	126.85(4)
S(1)#1-Ni(1)-Ni(2)#1	115.28(4)	S(3)-Ni(3)-Ni(2)	51.49(3)
S(2)-Ni(1)-Ni(2)#1	125.30(4)	S(5)#1-Ni(3)-Ni(2)	125.24(4)
S(2)#1-Ni(1)-Ni(2)#1	51.03(3)	S(4)-Ni(3)-Ni(2)	51.52(3)
Ni(2)-Ni(1)-Ni(2)#1	101.36(4)	Ni(3)#1-Ni(3)-Ni(2)	106.690(17)
S(3)-Ni(2)-S(2)	98.79(5)	C(1)-S(1)-Ni(1)	98.78(16)
S(3)-Ni(2)-S(4)	82.15(5)	C(1)-S(1)-Ni(2)#1	107.03(16)
S(2)-Ni(2)-S(4)	176.26(5)	Ni(1)-S(1)-Ni(2)#1	78.86(4)
S(3)-Ni(2)-S(1)#1	172.47(5)	C(2)-S(2)-Ni(1)	102.69(16)
S(2)-Ni(2)-S(1)#1	82.39(5)	C(2)-S(2)-Ni(2)	113.69(16)
S(4)-Ni(2)-S(1)#1	97.16(5)	Ni(1)-S(2)-Ni(2)	79.35(4)
S(3)-Ni(2)-Ni(3)	51.60(4)	C(3)-S(3)-Ni(2)	102.55(18)
S(2)-Ni(2)-Ni(3)	131.40(4)	C(3)-S(3)-Ni(3)	93.78(17)
S(4)-Ni(2)-Ni(3)	51.85(4)	Ni(2)-S(3)-Ni(3)	76.91(5)
S(1)#1-Ni(2)-Ni(3)	122.38(4)	C(4)-S(4)-Ni(2)	96.10(16)
S(3)-Ni(2)-Ni(1)	126.39(4)	C(4)-S(4)-Ni(3)	99.70(17)
S(2)-Ni(2)-Ni(1)	49.62(3)	Ni(2)-S(4)-Ni(3)	76.63(4)
S(4)-Ni(2)-Ni(1)	132.43(4)	C(5)-S(5)-Ni(3)	95.57(15)

S(1)#1-Ni(2)-Ni(1)	49.32(3)	C(5)-S(5)-Ni(3)#1	101.10(16)
Ni(3)-Ni(2)-Ni(1)	112.61(3)	Ni(3)-S(5)-Ni(3)#1	76.81(5)

Symmetry transformations used to generate equivalent atoms: #1 -x, y, -z+1/2

Table S7 the selected bond lengths (Å) and angles(°) for **2**.

Bond	Dist.(Å)	Bond	Dist.(Å)
Ni(1)-S(6)#1	2.193(3)	Ni(3)-S(6)	2.206(3)
Ni(1)-S(2)	2.193(3)	Ni(3)-S(5)	2.207(3)
Ni(1)-S(1)	2.202(3)	Ni(3)-Ni(1)#1	2.856(3)
Ni(1)-S(5)#1	2.215(3)	S(1)-C(1)	1.794(12)
Ni(1)-Ni(3)#1	2.856(3)	S(2)-C(6)	1.833(10)
Ni(2)-S(3)	2.197(3)	S(3)-C(11)	1.799(9)
Ni(2)-S(2)	2.201(3)	S(4)-C(16)	1.835(10)
Ni(2)-S(4)	2.201(3)	S(5)-C(21)	1.818(9)
Ni(2)-S(1)	2.214(3)	S(5)-Ni(1)#1	2.215(3)
Ni(2)-Ni(3)	2.929(2)	S(6)-C(26)	1.834(10)
Ni(3)-S(4)	2.200(3)	S(6)-Ni(1)#1	2.193(3)
Ni(3)-S(3)	2.201(3)		

Angle	(°)	Angle	(°)
S(6)#1-Ni(1)-S(2)	177.37(11)	S(3)-Ni(3)-Ni(1)#1	130.61(10)
S(6)#1-Ni(1)-S(1)	97.93(13)	S(6)-Ni(3)-Ni(1)#1	49.33(9)
S(2)-Ni(1)-S(1)	81.97(13)	S(5)-Ni(3)-Ni(1)#1	49.91(9)
S(6)#1-Ni(1)-S(5)#1	82.13(13)	S(4)-Ni(3)-Ni(2)	48.30(9)
S(2)-Ni(1)-S(5)#1	98.36(13)	S(3)-Ni(3)-Ni(2)	48.17(9)
S(1)-Ni(1)-S(5)#1	171.53(11)	S(6)-Ni(3)-Ni(2)	131.77(10)
S(6)#1-Ni(1)-Ni(3)#1	49.71(9)	S(5)-Ni(3)-Ni(2)	125.28(10)
S(2)-Ni(1)-Ni(3)#1	132.38(10)	Ni(1)#1-Ni(3)-Ni(2)	114.83(7)
S(1)-Ni(1)-Ni(3)#1	124.49(11)	C(1)-S(1)-Ni(1)	107.4(5)
S(5)#1-Ni(1)-Ni(3)#1	49.65(9)	C(1)-S(1)-Ni(2)	104.1(4)
S(3)-Ni(2)-S(2)	175.25(11)	Ni(1)-S(1)-Ni(2)	85.93(12)
S(3)-Ni(2)-S(4)	81.80(12)	C(6)-S(2)-Ni(1)	114.3(4)
S(2)-Ni(2)-S(4)	99.10(12)	C(6)-S(2)-Ni(2)	114.1(4)
S(3)-Ni(2)-S(1)	98.14(12)	Ni(1)-S(2)-Ni(2)	86.47(12)
S(2)-Ni(2)-S(1)	81.53(12)	C(11)-S(3)-Ni(2)	114.0(3)
S(4)-Ni(2)-S(1)	173.20(11)	C(11)-S(3)-Ni(3)	114.6(3)
S(3)-Ni(2)-Ni(3)	48.31(8)	Ni(2)-S(3)-Ni(3)	83.51(11)
S(2)-Ni(2)-Ni(3)	135.28(10)	C(16)-S(4)-Ni(3)	104.9(4)
S(4)-Ni(2)-Ni(3)	48.27(8)	C(16)-S(4)-Ni(2)	105.8(4)
S(1)-Ni(2)-Ni(3)	127.21(10)	Ni(3)-S(4)-Ni(2)	83.43(12)
S(4)-Ni(3)-S(3)	81.72(12)	C(21)-S(5)-Ni(3)	106.9(3)
S(4)-Ni(3)-S(6)	98.27(13)	C(21)-S(5)-Ni(1)#1	106.8(4)
S(3)-Ni(3)-S(6)	179.92(12)	Ni(3)-S(5)-Ni(1)#1	80.45(12)
S(4)-Ni(3)-S(5)	170.68(12)	C(26)-S(6)-Ni(1)#1	114.8(4)
S(3)-Ni(3)-S(5)	97.96(13)	C(26)-S(6)-Ni(3)	113.6(3)
S(6)-Ni(3)-S(5)	82.03(12)	Ni(1)#1-S(6)-Ni(3)	80.96(12)

S(4)-Ni(3)-Ni(1)#1	123.83(11)

Symmetry transformations used to generate equivalent atoms: #1 –x+2, -y+2, -z

Table S8 the selected bond lengths (Å) and angles(°) for **4**.

Bond	Dist.(Å)	Bond	Dist.(Å)
S(1)-C(1)	1.899(11)	S(5)-C(10)	1.858(18)
S(1)-Ni(2)	2.209(3)	S(5)-Ni(3)	2.195(4)
S(1)-Ni(1)	2.231(3)	S(5)-Ni(4)	2.212(4)
S(2)-C(5)	1.834(10)	S(6)-C(11)	1.877(11)
S(2)-Ni(2)	2.199(3)	S(6)-Ni(4)	2.224(4)
S(2)-Ni(1)	2.229(3)	S(6)-Ni(3)	2.225(3)
S(3)-C(8)	1.821(14)	Ni(1)-S(2)#1	2.229(3)
S(3)-Ni(3)	2.211(3)	Ni(1)-S(1)#1	2.231(3)
S(3)-Ni(2)	2.244(4)	Ni(2)-Ni(3)	2.857(3)
S(4)-C(7)	1.826(12)	Ni(4)-S(5)#1	2.212(4)
S(4)-Ni(2)	2.206(3)	Ni(4)-S(6)#1	2.224(4)
S(4)-Ni(3)	2.235(4)		
Angle	(°)	Angle	(°)
C(1)-S(1)-Ni(2)	111.6(4)	S(2)-Ni(2)-S(1)	82.80(11)
C(1)-S(1)-Ni(1)	112.9(4)	S(4)-Ni(2)-S(1)	172.43(11)
Ni(2)-S(1)-Ni(1)	86.11(9)	S(2)-Ni(2)-S(3)	178.78(12)
C(5)-S(2)-Ni(2)	113.6(4)	S(4)-Ni(2)-S(3)	78.35(12)
C(5)-S(2)-Ni(1)	114.4(4)	S(1)-Ni(2)-S(3)	97.97(12)
Ni(2)-S(2)-Ni(1)	86.38(10)	S(2)-Ni(2)-Ni(3)	130.69(10)
C(8)-S(3)-Ni(3)	114.7(5)	S(4)-Ni(2)-Ni(3)	50.42(9)
C(8)-S(3)-Ni(2)	115.6(5)	S(1)-Ni(2)-Ni(3)	122.24(9)
Ni(3)-S(3)-Ni(2)	79.75(12)	S(3)-Ni(2)-Ni(3)	49.62(9)
C(7)-S(4)-Ni(2)	112.6(3)	S(5)-Ni(3)-S(3)	99.98(14)
C(7)-S(4)-Ni(3)	113.9(4)	S(5)-Ni(3)-S(6)	83.08(12)
Ni(2)-S(4)-Ni(3)	80.05(13)	S(3)-Ni(3)-S(6)	172.50(12)
C(10)-S(5)-Ni(3)	114.7(5)	S(5)-Ni(3)-S(4)	178.22(12)
C(10)-S(5)-Ni(4)	114.4(5)	S(3)-Ni(3)-S(4)	78.44(12)
Ni(3)-S(5)-Ni(4)	86.29(11)	S(6)-Ni(3)-S(4)	98.59(12)
C(11)-S(6)-Ni(4)	111.9(4)	S(5)-Ni(3)-Ni(2)	129.99(11)
C(11)-S(6)-Ni(3)	116.2(4)	S(3)-Ni(3)-Ni(2)	50.63(9)
Ni(4)-S(6)-Ni(3)	85.26(11)	S(6)-Ni(3)-Ni(2)	122.32(9)
S(2)-Ni(1)-S(2)#1	175.64(14)	S(4)-Ni(3)-Ni(2)	49.53(9)
S(2)-Ni(1)-S(1)	81.64(10)	S(5)-Ni(4)-S(5)#1	175.71(16)
S(2)#1-Ni(1)-S(1)	98.88(10)	S(5)-Ni(4)-S(6)#1	97.75(12)
S(2)-Ni(1)-S(1)#1	98.88(10)	S(5)#1-Ni(4)-S(6)#1	82.70(11)
S(2)#1-Ni(1)-S(1)#1	81.64(10)	S(5)-Ni(4)-S(6)	82.70(11)
S(1)-Ni(1)-S(1)#1	166.43(14)	S(5)#1-Ni(4)-S(6)	97.75(12)
S(2)-Ni(2)-S(4)	101.00(12)	S(6)#1-Ni(4)-S(6)	167.97(14)

Symmetry transformations used to generate equivalent atoms: #1 –x, y, -z-1/2

Table S9 the selected bond lengths (Å) and angles(°) for **5**.

Bond	Dist.(Å)	Bond	Dist.(Å)
Ni(1)-S(5)#1	2.2028(14)	Ni(3)-Ni(4)	2.9895(9)
Ni(1)-S(5)	2.2028(14)	Ni(4)-S(7)#1	2.1545(19)
Ni(1)-S(8)	2.2277(15)	Ni(4)-S(10)	2.1928(18)
Ni(1)-S(8)#1	2.2277(15)	Ni(4)-S(9)	2.2061(17)
Ni(2)-S(5)	2.1709(16)	Ni(4)-S(6)	2.2091(18)
Ni(2)-S(6)	2.1873(17)	S(5)-C(10)	1.826(6)
Ni(2)-S(10)	2.1931(18)	S(6)-C(9)	1.809(7)
Ni(2)-S(8)#1	2.2018(17)	S(7)-C(8)	1.884(10)
Ni(2)-Ni(4)	2.6903(11)	S(7)-Ni(4)#1	2.1545(19)
Ni(3)-S(7)	2.1974(16)	S(8)-C(5)	1.776(6)
Ni(3)-S(7)#1	2.1974(16)	S(8)-Ni(2)#1	2.2018(17)
Ni(3)-S(9)#1	2.2322(16)	S(9)-C(6)	1.791(6)
Ni(3)-S(9)	2.2322(16)	S(10)-C(20)	1.778(8)
Ni(3)-Ni(4)#1	2.9895(9)		
Angle	(º)	Angle	(º)
S(5)#1-Ni(1)-S(5)	175.26(9)	S(7)#1-Ni(4)-Ni(2)	120.16(6)
S(5)#1-Ni(1)-S(8)	84.62(5)	S(10)-Ni(4)-Ni(2)	52.17(5)
S(5)-Ni(1)-S(8)	95.66(5)	S(9)-Ni(4)-Ni(2)	122.95(5)
S(5)#1-Ni(1)-S(8)#1	95.66(5)	S(6)-Ni(4)-Ni(2)	51.91(5)
S(5)-Ni(1)-S(8)#1	84.62(5)	S(7)#1-Ni(4)-Ni(3)	47.21(5)
S(8)-Ni(1)-S(8)#1	173.24(9)	S(10)-Ni(4)-Ni(3)	124.82(7)
S(5)-Ni(2)-S(6)	90.93(6)	S(9)-Ni(4)-Ni(3)	48.03(4)
S(5)-Ni(2)-S(10)	169.53(7)	S(6)-Ni(4)-Ni(3)	136.77(5)
S(6)-Ni(2)-S(10)	80.25(7)	Ni(2)-Ni(4)-Ni(3)	111.73(3)
S(5)-Ni(2)-S(8)#1	86.01(6)	C(10)-S(5)-Ni(2)	98.5(2)
S(6)-Ni(2)-S(8)#1	171.96(7)	C(10)-S(5)-Ni(1)	109.3(2)
S(10)-Ni(2)-S(8)#1	101.98(7)	Ni(2)-S(5)-Ni(1)	86.69(6)
S(5)-Ni(2)-Ni(4)	117.77(5)	C(9)-S(6)-Ni(2)	104.1(2)
S(6)-Ni(2)-Ni(4)	52.64(5)	C(9)-S(6)-Ni(4)	115.4(2)
S(10)-Ni(2)-Ni(4)	52.16(5)	Ni(2)-S(6)-Ni(4)	75.45(6)
S(8)#1-Ni(2)-Ni(4)	122.76(5)	C(8)-S(7)-Ni(4)#1	97.8(3)
S(7)-Ni(3)-S(7)#1	171.94(11)	C(8)-S(7)-Ni(3)	110.1(3)
S(7)-Ni(3)-S(9)#1	83.66(6)	Ni(4)#1-S(7)-Ni(3)	86.77(6)
S(7)#1-Ni(3)-S(9)#1	96.81(6)	C(5)-S(8)-Ni(2)#1	106.7(2)
S(7)-Ni(3)-S(9)	96.81(6)	C(5)-S(8)-Ni(1)	103.7(2)
S(7)#1-Ni(3)-S(9)	83.66(6)	Ni(2)#1-S(8)-Ni(1)	85.33(6)
S(9)#1-Ni(3)-S(9)	173.40(9)	C(6)-S(9)-Ni(4)	104.06(19)
S(7)-Ni(3)-Ni(4)#1	46.02(5)	C(6)-S(9)-Ni(3)	104.7(2)
S(7)#1-Ni(3)-Ni(4)#1	138.38(5)	Ni(4)-S(9)-Ni(3)	84.68(6)

S(9)#1-Ni(3)-Ni(4)#1	47.29(4)	C(20)-S(10)-Ni(4)	104.1(3)
S(9)-Ni(3)-Ni(4)#1	129.40(5)	C(20)-S(10)-Ni(2)	115.9(3)
S(7)-Ni(3)-Ni(4)	138.38(5)	Ni(4)-S(10)-Ni(2)	75.67(6)
S(7)#1-Ni(3)-Ni(4)	46.02(5)	S(7)#1-Ni(4)-S(9)	85.29(7)
S(9)#1-Ni(3)-Ni(4)	129.40(5)	S(10)-Ni(4)-S(9)	171.27(7)
S(9)-Ni(3)-Ni(4)	47.29(4)	S(7)#1-Ni(4)-S(6)	170.94(7)
Ni(4)#1-Ni(3)-Ni(4)	135.55(5)	S(10)-Ni(4)-S(6)	79.78(7)
S(7)#1-Ni(4)-S(10)	91.64(8)	S(9)-Ni(4)-S(6)	102.77(7)

Symmetry transformations used to generate equivalent atoms: #1 –x+3/2, y, -z+1/2

Table S10 the selected bond lengths (Å) and angles(°) for **6**.

Bond	Dist.(Å)	Bond	Dist.(Å)
Ni(1)-S(1)#1	2.191(2)	Ni(3)-S(5)	2.211(2)
Ni(1)-S(1)	2.191(2)	Ni(3)-Ni(4)	2.9593(15)
Ni(1)-S(2)	2.191(2)	Ni(4)-S(6)	2.184(2)
Ni(1)-S(2)#1	2.191(2)	Ni(4)-S(6)#1	2.184(2)
Ni(1)-Ni(2)	2.9439(15)	Ni(4)-S(5)	2.215(2)
Ni(1)-Ni(2)#1	2.9439(15)	Ni(4)-S(5)#1	2.215(2)
Ni(2)-S(1)	2.156(2)	Ni(4)-Ni(3)#1	2.9593(15)
Ni(2)-S(3)	2.180(2)	S(1)-C(3)	1.814(8)
Ni(2)-S(4)	2.196(2)	S(2)-C(4)	1.771(7)
Ni(2)-S(2)	2.214(2)	S(3)-C(1)	1.829(8)
Ni(2)-Ni(3)	2.794(2)	S(4)-C(10)	1.816(8)
Ni(3)-S(6)	2.163(2)	S(5)-C(13)	1.786(8)
Ni(3)-S(4)	2.176(2)	S(6)-C(12)	1.789(8)
Ni(3)-S(3)	2.205(2)		
Angle	(º)	Angle	(º)
S(1)#1-Ni(1)-S(1)	165.44(12)	S(5)-Ni(3)-Ni(2)	123.31(6)
S(1)#1-Ni(1)-S(2)	99.13(7)	S(6)-Ni(3)-Ni(4)	47.40(6)
S(1)-Ni(1)-S(2)	82.50(7)	S(4)-Ni(3)-Ni(4)	129.17(6)
S(1)#1-Ni(1)-S(2)#1	82.50(7)	S(3)-Ni(3)-Ni(4)	135.41(7)
S(1)-Ni(1)-S(2)#1	99.13(7)	S(5)-Ni(3)-Ni(4)	48.11(5)
S(2)-Ni(1)-S(2)#1	167.23(11)	Ni(2)-Ni(3)-Ni(4)	116.12(4)
S(1)#1-Ni(1)-Ni(2)	142.29(6)	S(6)-Ni(4)-S(6)#1	168.03(12)
S(1)-Ni(1)-Ni(2)	46.88(6)	S(6)-Ni(4)-S(5)	80.96(8)
S(2)-Ni(1)-Ni(2)	48.41(5)	S(6)#1-Ni(4)-S(5)	100.14(8)
S(2)#1-Ni(1)-Ni(2)	124.71(6)	S(6)-Ni(4)-S(5)#1	100.14(8)
S(1)#1-Ni(1)-Ni(2)#1	46.88(6)	S(6)#1-Ni(4)-S(5)#1	80.96(8)
S(1)-Ni(1)-Ni(2)#1	142.29(6)	S(5)-Ni(4)-S(5)#1	169.61(12)
S(2)-Ni(1)-Ni(2)#1	124.71(6)	S(6)-Ni(4)-Ni(3)	46.80(5)
S(2)#1-Ni(1)-Ni(2)#1	48.41(5)	S(6)#1-Ni(4)-Ni(3)	140.93(6)
Ni(2)-Ni(1)-Ni(2)#1	129.77(6)	S(5)-Ni(4)-Ni(3)	47.97(6)
S(1)-Ni(2)-S(3)	100.41(9)	S(5)#1-Ni(4)-Ni(3)	126.14(7)
S(1)-Ni(2)-S(4)	177.07(8)	S(6)-Ni(4)-Ni(3)#1	140.93(6)

S(3)-Ni(2)-S(4)	78.75(8)	S(6)#1-Ni(4)-Ni(3)#1	46.80(5)
S(1)-Ni(2)-S(2)	82.75(8)	S(5)-Ni(4)-Ni(3)#1	126.14(7)
S(3)-Ni(2)-S(2)	169.74(8)	S(5)#1-Ni(4)-Ni(3)#1	47.97(6)
S(4)-Ni(2)-S(2)	98.56(8)	Ni(3)-Ni(4)-Ni(3)#1	127.69(6)
S(1)-Ni(2)-Ni(3)	131.52(7)	C(3)-S(1)-Ni(2)	114.4(3)
S(3)-Ni(2)-Ni(3)	50.80(6)	C(3)-S(1)-Ni(1)	114.1(3)
S(4)-Ni(2)-Ni(3)	49.95(6)	Ni(2)-S(1)-Ni(1)	85.25(7)
S(2)-Ni(2)-Ni(3)	120.07(6)	C(4)-S(2)-Ni(1)	105.8(3)
S(1)-Ni(2)-Ni(1)	47.87(6)	C(4)-S(2)-Ni(2)	113.3(3)
S(3)-Ni(2)-Ni(1)	128.33(7)	Ni(1)-S(2)-Ni(2)	83.85(7)
S(4)-Ni(2)-Ni(1)	134.74(6)	C(1)-S(3)-Ni(2)	114.5(3)
S(2)-Ni(2)-Ni(1)	47.74(6)	C(1)-S(3)-Ni(3)	114.6(3)
Ni(3)-Ni(2)-Ni(1)	114.70(4)	Ni(2)-S(3)-Ni(3)	79.17(8)
S(6)-Ni(3)-S(4)	100.52(9)	C(10)-S(4)-Ni(3)	114.3(3)
S(6)-Ni(3)-S(3)	176.73(8)	C(10)-S(4)-Ni(2)	113.6(3)
S(4)-Ni(3)-S(3)	78.66(8)	Ni(3)-S(4)-Ni(2)	79.46(8)
S(6)-Ni(3)-S(5)	81.53(8)	C(13)-S(5)-Ni(3)	106.8(2)
S(4)-Ni(3)-S(5)	173.08(8)	C(13)-S(5)-Ni(4)	103.2(3)
S(3)-Ni(3)-S(5)	99.65(8)	Ni(3)-S(5)-Ni(4)	83.92(7)
S(6)-Ni(3)-Ni(2)	131.71(7)	C(12)-S(6)-Ni(3)	113.9(3)
S(4)-Ni(3)-Ni(2)	50.60(6)	C(12)-S(6)-Ni(4)	113.5(3)
S(3)-Ni(3)-Ni(2)	50.03(6)	Ni(3)-S(6)-Ni(4)	85.79(8)

Symmetry transformations used to generate equivalent atoms: #1 –x+3/2, - y-1/2, z

Table S11 the crystal data for culster **3**.

Compound	**3**
Crystal appearance	black prism
Crystal Size (mm)	0.4×0.20×0.20
a (Å)	13.677(2)
b (Å)	13.672(1)
c (Å)	22.446(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	4197(1)