Supplementary Information

In situ synthesis of nickel tiara-like clusters with two different thiolate bridges

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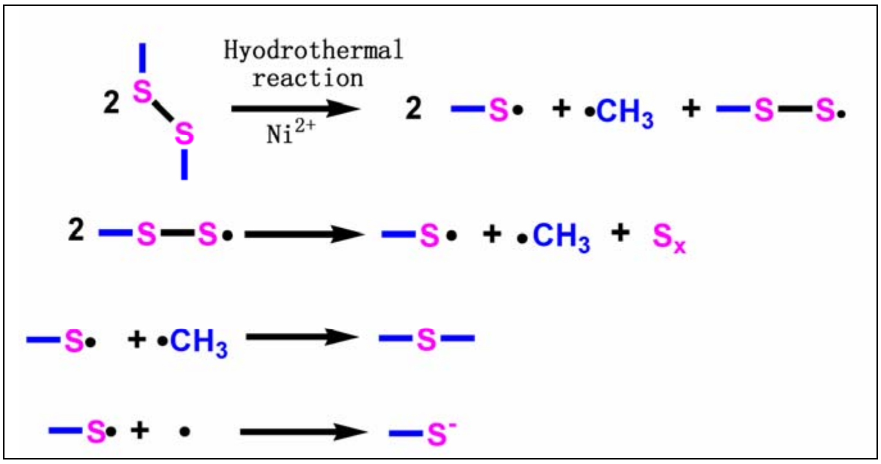
Scheme S1. Mechanism of the in situ syntheses of methanethiol (the same goes for ethanethiol).



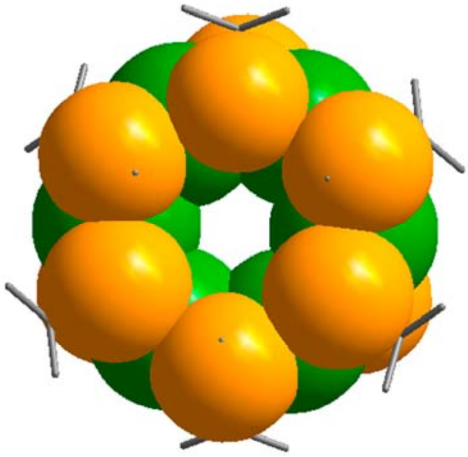


Fig. S1 Molecular view of **1** in space filling model. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

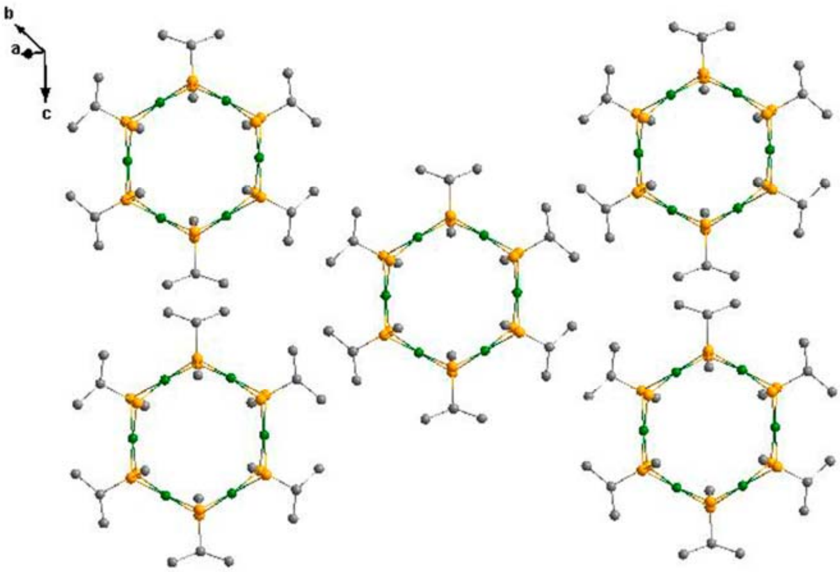


Fig. S2 Crystal packing pattern of **1**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

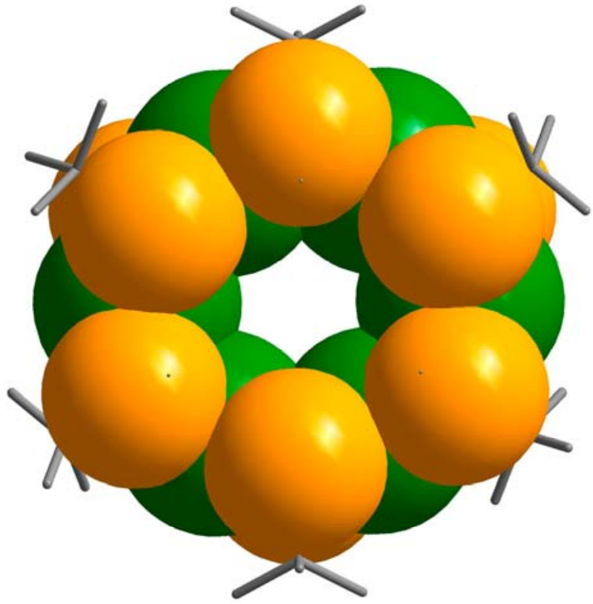


Fig. S3 Molecular view of **2** in space filling model. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

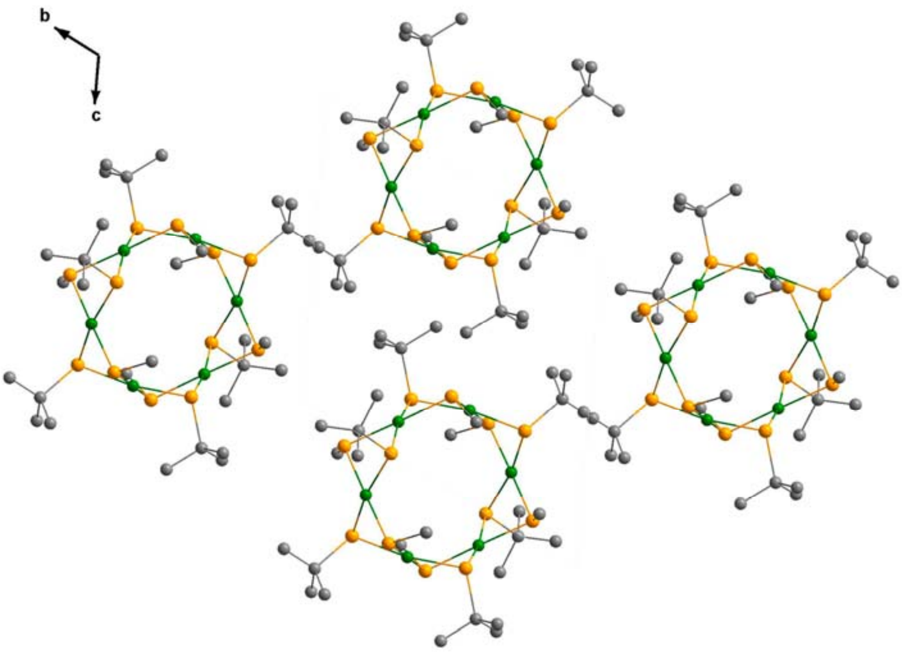


Fig. S4 Crystal packing pattern of **2**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

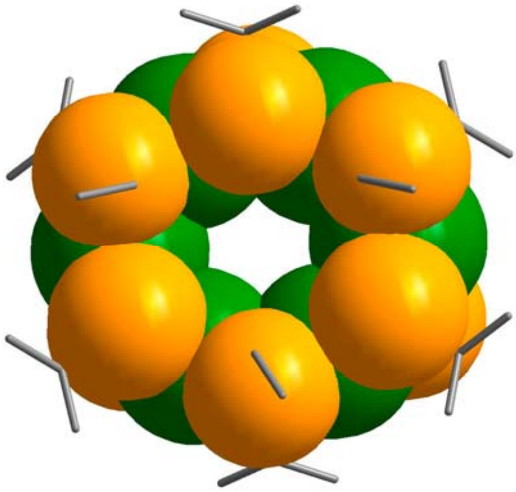


Fig. S5 Molecular view of **3** in space filling model. The hydrogen atoms and the distored carbon are omitted for clarity (Ni green, S yellow, C gray).

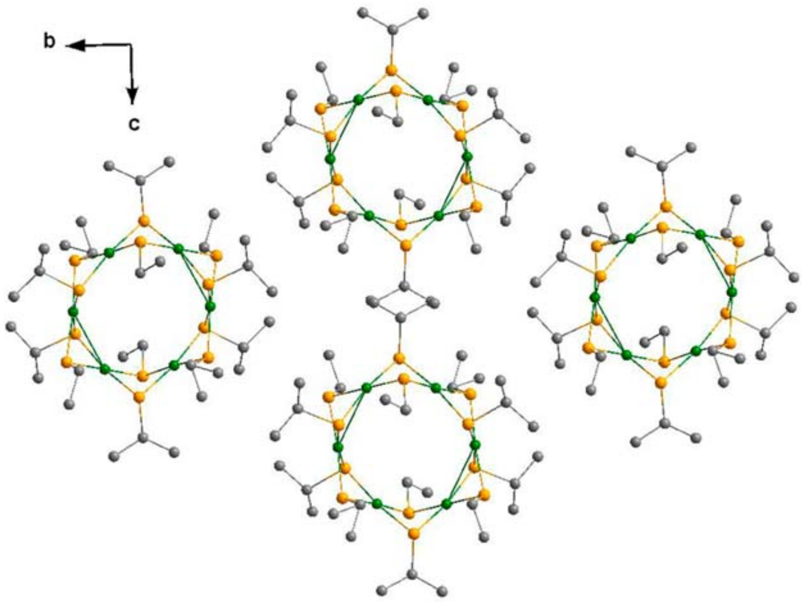


Fig. S6 Crystal packing pattern of **3**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

Electronic Supplementary Material (ESI) for Dalton Transactions

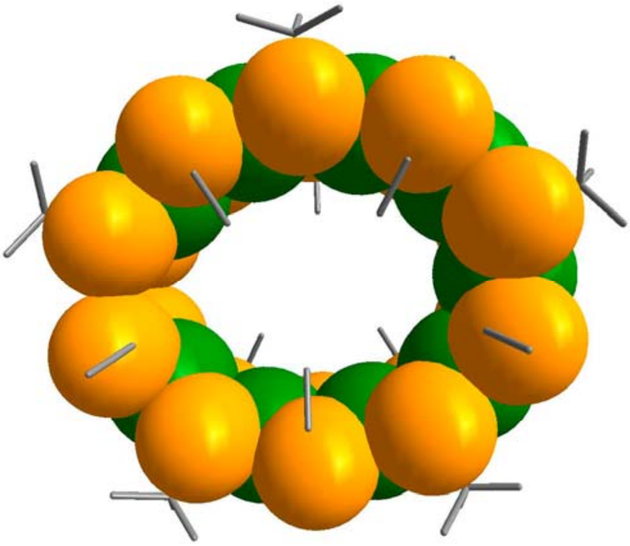


Fig. S7 Molecular view of **4** in space filling model. The hydrogen atoms and the distorted carbon are omitted for clarity (Ni green, S yellow, C gray).

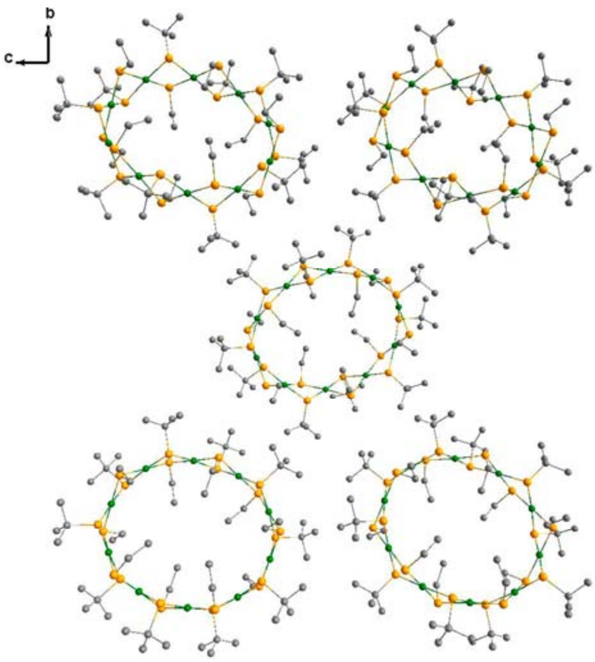


Fig. S8 Crystal packing pattern of **4**. The hydrogen atoms are omitted for clarity (Ni green, S yellow, C gray).

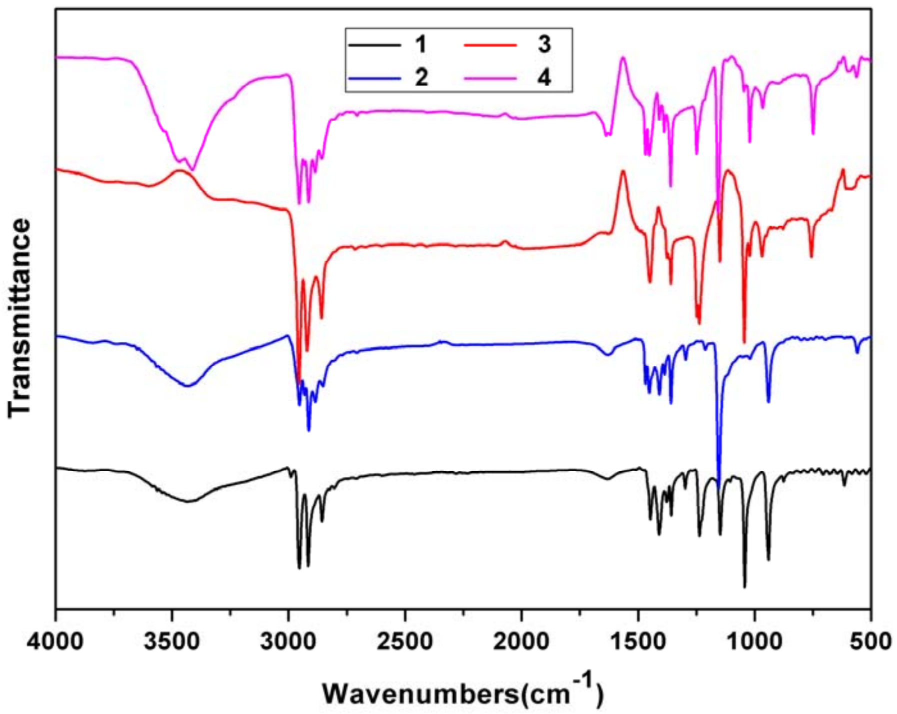


Fig. S9 IR spectra of compounds **1**, **2**, **3** and **4**.

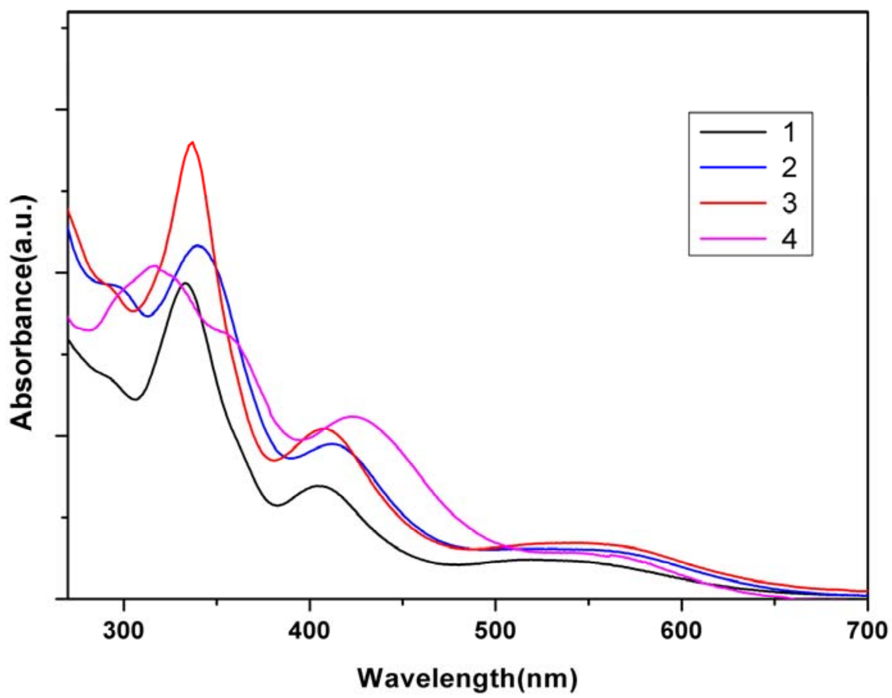


Fig. S10 UV-vis-NIR spectra of compounds **1**, **2**, **3** and **4**.

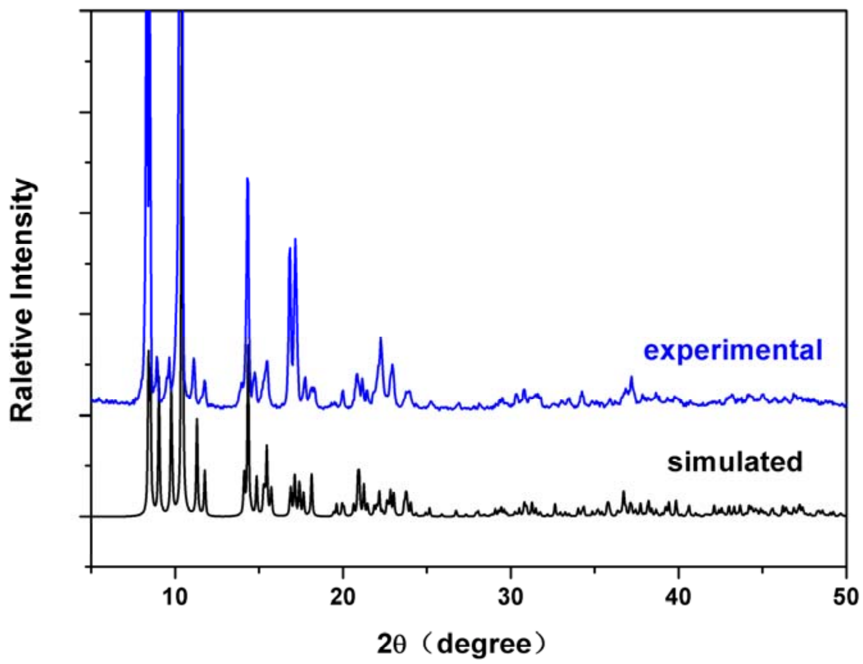


Fig. S11 Powder X-ray diffractions for simulated and experimental **1**.

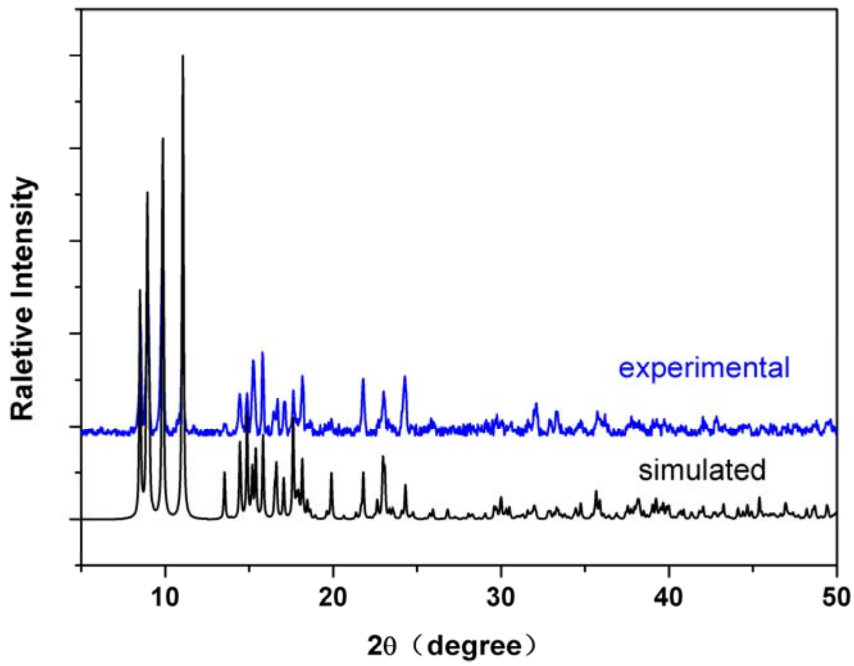


Fig. S12 Powder X-ray diffractions for simulated and experimental **2**.

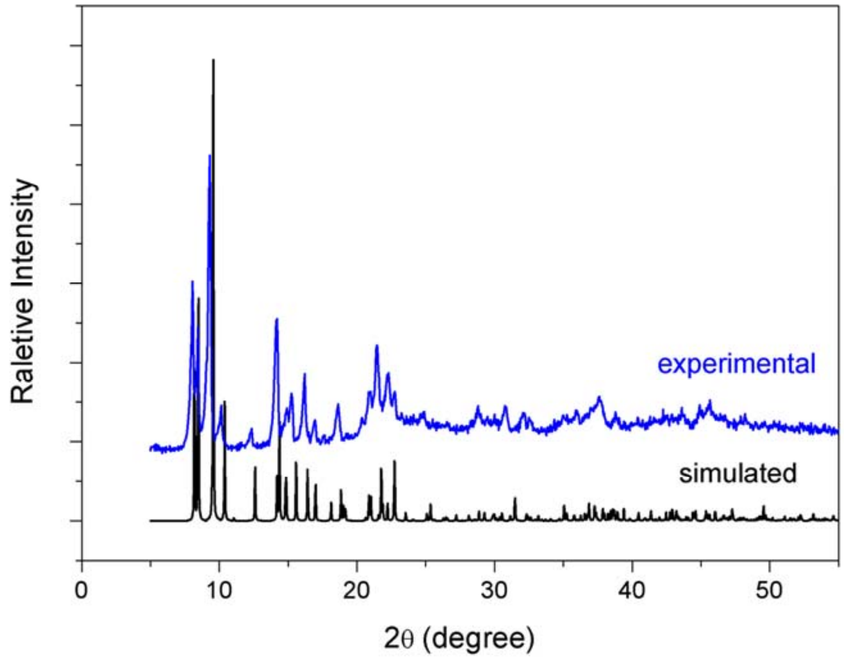


Fig. S13 Powder X-ray diffractions for simulated and experimental **3**.

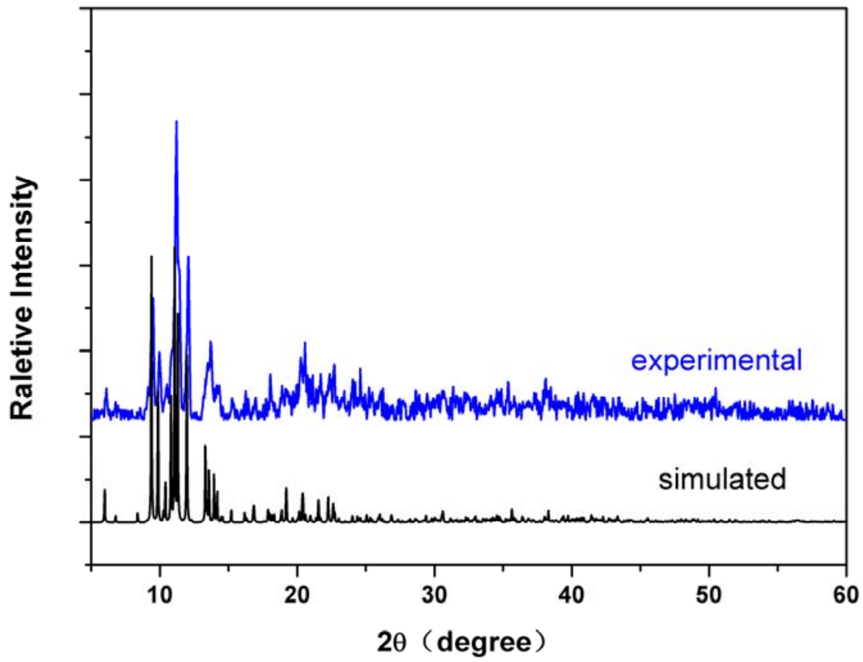


Fig. S14 Powder X-ray diffractions for simulated and experimental **4**.

Table S1 The selected bond length (Å) and angles (deg.) for complexes **1**.

Ni(1)-S(5)#1	2.194(3)	Ni(3)-S(5)	2.190(3)
Ni(1)-S(1)	2.195(3)	Ni(3)-S(6)	2.211(3)
Ni(1)-S(6)#1	2.209(3)	Ni(3)-S(4)	2.211(3)
Ni(1)-S(2)	2.211(3)	S(5)-Ni(1)#1	2.194(3)
Ni(2)-S(3)	2.192(3)	S(6)-Ni(1)#1	2.209(3)
Ni(2)-S(1)	2.197(3)	Ni(1)-Ni(3)#1	2.923(3)
Ni(2)-S(4)	2.211(3)	Ni(1)-Ni(2)	2.955(2)
Ni(2)-S(2)	2.214(3)	Ni(2)-Ni(3)	2.917(2)
Ni(3)-S(3)	2.189(3)	Ni(3)-Ni(1)#1	2.923(3)
Ni(1)-S(1)-Ni(2)	84.52(11)	Ni(3)-S(4)-Ni(2)	82.51(8)
Ni(1)-S(2)-Ni(2)	83.79(11)	Ni(3)-S(5)-Ni(1)#1	83.60(9)
Ni(3)-S(3)-Ni(2)	83.46(10)	Ni(1)#1-S(6)-Ni(3)	82.79(7)

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

Table S2 The selected bond length (Å) and angles (deg.) for complexes **2**.

Ni(1)-S(5)#1	2.190(2)	Ni(3)-S(5)	2.201(29)
Ni(1)-S(6)#1	2.202(2)	Ni(3)-S(6)	2.199(2)
Ni(1)-S(1)	2.202(2)	Ni(3)-S(3)	2.201(2)
Ni(1)-S(2)	2.208(2)	S(5)-Ni(1)#1	2.190(2)
Ni(2)-S(4)	2.197(2)	S(6)-Ni(1)#1	2.201(2)
Ni(2)-S(1)	2.200(2)	Ni(3)-S(4)	2.1944(2)
Ni(2)-S(3)	2.200(2)	Ni(1)-Ni(2)	2.887(3)
Ni(2)-S(2)	2.208(2)	Ni(2)-Ni(3)	3.006(4)
Ni(2)-S(1)-Ni(1)	82.00(7)	Ni(3)-S(4)-Ni(2)	84.46(7)
Ni(1)-S(2)-Ni(2)	81.72(6)	Ni(1)#1-S(5)-Ni(3)	86.47(7)
Ni(2)-S(3)-Ni(3)	84.20(6)	Ni(3)-S(6)-Ni(1)#1	86.22(7)

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

Table S3 The selected bond length (Å) and angles (deg.) for complexes **3**.

Ni(1)-S(2)	2.192(3)	S(3)-Ni(3)#1	2.194(2)
Ni(1)-S(6)	2.197(3)	S(4)-Ni(3)#1	2.216(2)
Ni(1)-S(5)	2.202(3)	Ni(3)-S(6)	2.195(2)
Ni(1)-S(1)	2.212(3)	Ni(3)-S(5)	2.212(3)
Ni(2)-S(3)	2.194(2)	Ni(3)-S(4)#1	2.216(2)
Ni(2)-S(2)	2.197(2)	Ni(1)-Ni(2)	2.860(2)
Ni(2)-S(4)	2.208(2)	Ni(2)-Ni(3)	2.882(2)
Ni(2)-S(1)	2.214(3)	Ni(3)-Ni(1)	3.035(2)
Ni(3)-S(3)#1	2.194(2)		
Ni(1)-S(1)-Ni(2)	80.49(9)	Ni(2)-S(4)-Ni(3)#1	81.31(9)
Ni(1)-S(2)-Ni(2)	81.30(8)	Ni(1)-S(5)-Ni(3)	86.87(9)
Ni(2)-S(3)-Ni(3)#1	82.11(9)	Ni(3)-S(6)-Ni(1)	87.39(9)

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

Table S4 The selected bond length (Å) and angles (deg.) for complexes **4**.

Ni(1)-S(10)#1	2.199(3)	Ni(4)-S(5)	2.204(3)
Ni(1)-S(2)	2.202(3)	Ni(4)-S(6)	2.210(3)
Ni(1)-S(1)	2.206(3)	Ni(5)-S(10)	2.191(3)
Ni(1)-S(9)#1	2.213(3)	Ni(5)-S(8)	2.194(3)
Ni(2)-S(2)	2.190(3)	Ni(5)-S(7)	2.215(3)
Ni(2)-S(4)	2.193(3)	Ni(5)-S(9)	2.229(3)
Ni(2)-S(3)	2.207(3)	S(9)-Ni(1)#1	2.213(3)
Ni(2)-S(1)	2.214(3)	S(10)-Ni(1)#1	2.199(3)
Ni(3)-S(4)	2.197(3)	Ni(1)-Ni(2)	3.188(3)
Ni(3)-S(3)	2.200(3)	Ni(2)-Ni(3)	3.085(1)
Ni(3)-S(6)	2.206(3)	Ni(3)-Ni(4)	3.088(3)
Ni(3)-S(5)	2.207(3)	Ni(4)-Ni(5)	3.166(2)
Ni(4)-S(8)	2.192(3)	Ni(5)-Ni(1)#1	3.212(3)
Ni(4)-S(7)	2.195(3)		
Ni(1)-S(1)-Ni(2)	92.30(10)	Ni(3)-S(6)-Ni(4)	88.76(10)
Ni(2)-S(2)-Ni(1)	93.07(10)	Ni(4)-S(7)-Ni(5)	91.74(10)
Ni(3)-S(3)-Ni(2)	88.85(9)	Ni(4)-S(8)-Ni(5)	92.41(11)
Ni(2)-S(4)-Ni(3)	89.30(9)	Ni(1)#1-S(9)-Ni(5)	92.60(10)
Ni(4)-S(5)-Ni(3)	88.88(10)	Ni(5)-S(10)-Ni(1)#1	94.03(10)

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