Electronic Supplementary Material (ESI) for Chemical Communications

-Electronic Supplementary Information-

First Magnets Based on Thiocyanato-Bridges

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Data collection and structure refinement

X-ray intensity data were collected with Mo-*Kα* radiation (wavelength = 0.71073 Å) with a Bruker-AXS kappa APEX II Quazar diffractometer by using φ and *ω* scans and a 30-W air-cooled microfocus source with focusing multilayer optics at a temperature of 100 K. Multiscan absorption corrections were applied. The structure was solved using SUPERFLIP,[1] and refined by means of least-squares procedures on F using the programs of the PC version of CRYSTALS.[2] Atomic scattering factors were taken from the International tables for X-ray crystallography.[3] Hydrogen atoms were refined with riding constraints. The data were refined as a two-component twin, (1 0 0, 0 1 0, 0 0 1) and (0 -0.5 -0.5,-1 -0.5 0.5, -1 0.5 -0.5), with twin element scale factors of 0.5170(12) and 0.4830(12). The three L^{N4} ligands were totally or partially disordered over two positions (occupancy ratio 0.5:0.5).

We used different types of restraints for the two disordered macrocyclic ligands bonded to Ni1 and Ni2 :

- geometrical restraints, using the command SAME: This commands permits to have equivalent geometries for the two disordered parts of the two ligands
- Restraints on anisotropic displacement parameters, using the commands SIMU and DELU. They take into account that atoms, which are bound to one another, move similarly, both in direction and amount.
- U(IJ) used to ensure that the vibration parameters of adjacent atoms are similar.

Table S1 Crystallographic and refinement data for **1**

Empirical formula	$C_{57}\ H_{66}\ Mo_2\ N_{24}\ Ni_3\ S_{12}$
Formula weight	1840.12
Temperature	100K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 12.5105(10) Å α = 90.419(4)° b= 16.4003(13) Å β = 94.755(4)° c= 19.0260(15) Å γ = 108.682(4)°
Volume	3682.9(5) $Å^3$
Z	2
Density (calculated)	1.659
Absorption coefficient	1.480 mm^{-1}
F(000)	1872.00
Crystal size	0.10 x 0.10 x 0.25 mm^3
Theta range for data collection	1.075 to 28.402°
Index ranges	-16<=h<=+16;-21<=h<=+18;-25<=h<=+25
Reflections collected	56578
Independent reflections	17765 (Rint = 0.061)
Absorption correction	Multi-scan
Refinement method	Least squares procedures on F
Data / restraints / parameters	10632 / 1039 / 1244
Goodness-of-fit on F	1.1302
Final R indices [I> 2σ]	R1= 0.0666; wR2 = 0.0669
R indices (all data)	R1= 0.1254; wR2 = 0.1120
Largest diff. peak and hole	-0.86 and +1.70 e. $Å^{-3}$

$R = \Sigma[//Fo/-/Fc//]/\Sigma[/Fo/]$

$wR2 = (\Sigma[\ w(i)*D'(i)*D'(i]/\Sigma[\ w(i)*Fo(i)*Fo(i)])^{1/2}$

$D' = Fo-Fc$

[1] L. Palatinus, G. Chapuis, *J. Appl. Cryst.,* 2007, **40**, 786

[2] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Crystallogr.,*2003, **36**, 1487

[3] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Figure S1 Ortep view of the asymmetric unit in **1** showing all the disordered positions with ellipsoids cut at the 30% level. The atom labels are given for the two $\{Mo(NCS)_6\}$ units. The figure shows the two disordered positions for the L^{N4} ligands (H atoms have been omitted for clarity)

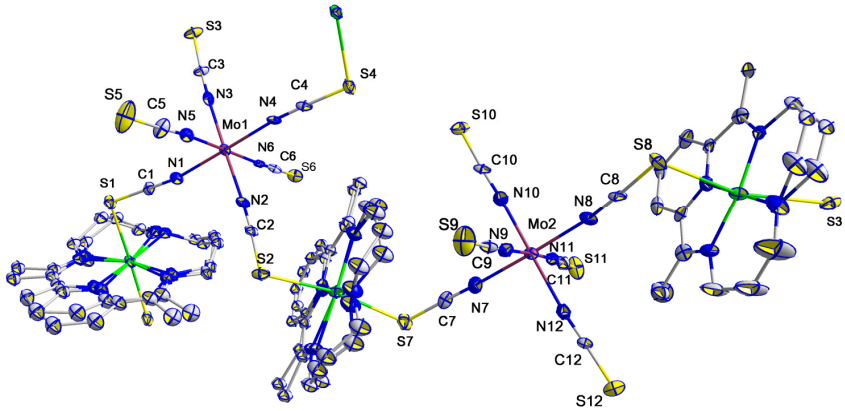


Figure S2 Ortep view of the asymmetric unit of **1** with ellipsoids cut at the 30% level. The atom labels and one of the two disordered positions are given for the three $\{NiL^{N4}\}$ units (H atoms have been omitted for clarity).

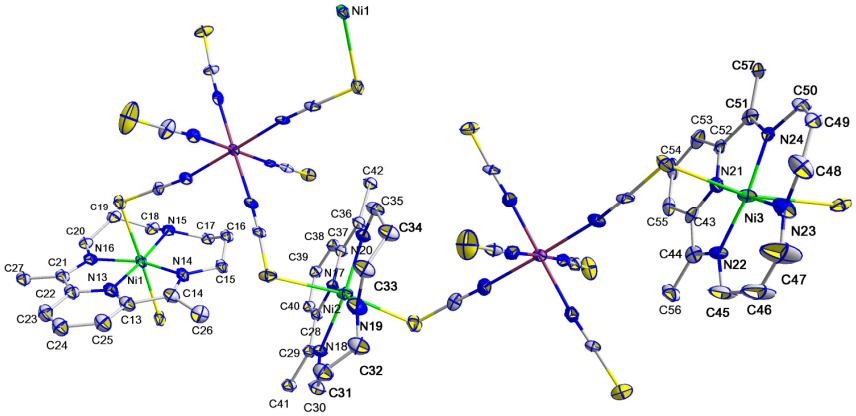


Figure S3 Ortep view of the asymmetric unit of **1** with ellipsoids cut at the 30% level. The atom labels and the second disordered positions are given for the three $\{NiL^{N4}\}$ units (H atoms have been omitted for clarity).

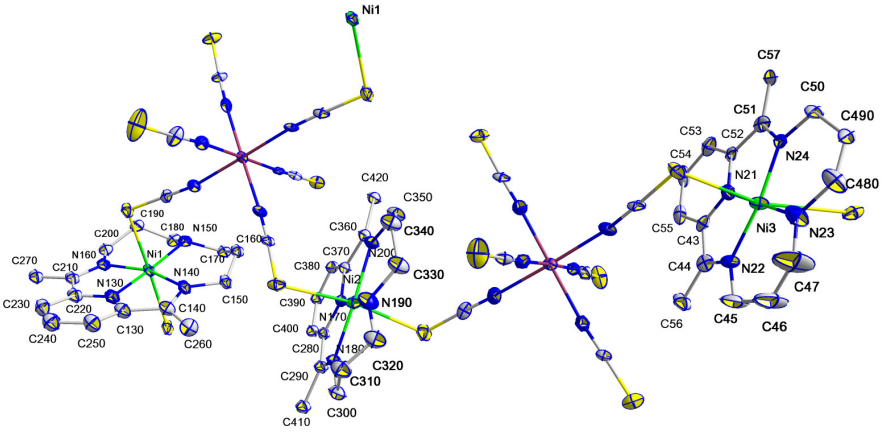


Table S2 Selected Bond distances (Å) for **1**

Mo1	N1	2.124(7)Å		Mo1	N2	2.093(8)Å
Mo1	N3	2.081(8)Å		Mo1	N4	2.101(7)Å
Mo1	N5	2.068(7)Å		Mo1	N6	2.094(7)Å
Mo2	N7	2.125(8)Å		Mo2	N8	2.113(8)Å
Mo2	N9	2.078(7)Å		Mo2	N10	2.066(8)Å
Mo2	N11	2.098(7)Å		Mo2	N12	2.093(8)Å
Ni1	S1	2.593(2)Å		Ni1	S4 1_455	2.531(3)Å
Ni1	N15	2.005(17)Å		Ni1	N150	2.024(17)Å
Ni1	N14	2.017(8)Å		Ni1	N140	2.055(8)Å
Ni1	N130	1.923(9)Å		Ni1	N13	1.910(8)Å
Ni1	N160	2.000(8)Å		Ni1	N16	2.054(8)Å
Ni2	S2	2.574(3)Å		Ni2	S7	2.591(3)Å
Ni2	N18	2.117(7)Å		Ni2	N180	1.988(7)Å
Ni2	N170	1.880(8)Å		Ni2	N17	1.957(7)Å
Ni2	N200	2.081(8)Å		Ni2	N20	1.980(8)Å
Ni2	N19	1.870(10)Å		Ni2	N190	2.129(13)Å

Ni3	S8	2.887(3)Å		Ni3	N21	1.829(7)Å
Ni3	N22	1.947(7)Å		Ni3	N23	1.938(8)Å
Ni3	N24	1.934(7)Å		Ni3	S8	2.887(3)Å
C1	N1	1.155(11)Å		C1	S1	1.642(9)Å
C2	N2	1.162(12)Å		C2	S2	1.640(10)Å
C3	N3	1.174(11)Å		C3	S3	1.600(8)Å
C4	N4	1.166(11)Å		C4	S4	1.646(9)Å
C5	N5	1.177(10)Å		C5	S5	1.621(8)Å
C6	N6	1.195(10)Å		C6	S6	1.607(7)Å
C7	N7	1.148(12)Å		C7	S7	1.646(9)Å
C8	N8	1.194(12)Å		C8	S8	1.627(9)Å
C9	N9	1.166(11)Å		C9	S9	1.618(9)Å
C10	N10	1.168(12)Å		C10	S10	1.629(10)Å
C11	N11	1.150(11)Å		C11	S11	1.632(10)Å
C12	N12	1.163(12)Å		C12	S12	1.605(10)Å

Table S3 Selected Bond Angles (°) for **1**

N1	Mo1	N2	91.5(2)°	N1	Mo1	N3	89.6(3)°
N2	Mo1	N3	178.8(3)°	N1	Mo1	N4	179.4(3)°
N2	Mo1	N4	88.7(3)°	N3	Mo1	N4	90.1(3)°
N1	Mo1	N5	87.9(3)°	N2	Mo1	N5	89.5(3)°
N3	Mo1	N5	90.4(3)°	N4	Mo1	N5	91.6(3)°
N1	Mo1	N6	91.4(2)°	N2	Mo1	N6	90.7(3)°
N3	Mo1	N6	89.4(3)°	N4	Mo1	N6	89.1(3)°
N5	Mo1	N6	179.3(3)°	N7	Mo2	N8	177.9(3)°
N7	Mo2	N9	88.5(3)°	N8	Mo2	N9	91.5(3)°
N7	Mo2	N10	87.9(3)°	N8	Mo2	N10	90.0(3)°
N9	Mo2	N10	88.6(3)°	N7	Mo2	N11	88.9(3)°
N8	Mo2	N11	91.1(3)°	N9	Mo2	N11	177.3(3)°
N10	Mo2	N11	92.0(3)°	N7	Mo2	N12	92.3(3)°
N8	Mo2	N12	89.8(3)°	N9	Mo2	N12	90.8(3)°
N10	Mo2	N12	179.4(3)°	N11	Mo2	N12	88.5(3)°
S1	Ni1	S4 1_455	176.46(1)°	S1	Ni1	N15	90.0(6)°
S4 1_455	Ni1	N15	93.4(5)°	S1	Ni1	N150	91.6(5)°
S4 1_455	Ni1	N150	91.6(5)°	N15	Ni1	N150	10.7(4)°
S1	Ni1	N14	93.4(7)°	S4 1_455	Ni1	N14	85.1(8)°
N15	Ni1	N14	101.6(4)°	N150	Ni1	N14	90.9(4)°
S1	Ni1	N140	91.3(7)°	S4 1_455	Ni1	N140	86.7(7)°
N15	Ni1	N140	110.6(4)°	N150	Ni1	N140	100.4(4)°
N14	Ni1	N140	9.3(4)°	S1	Ni1	N130	84.4(8)°
S4 1_455	Ni1	N130	92.4(8)°	N15	Ni1	N130	169.0(5)°
N150	Ni1	N130	175.8(9)°	N14	Ni1	N130	88.2(4)°
S1	Ni1	N13	85.9(8)°	S4 1_455	Ni1	N13	90.7(8)°
N15	Ni1	N13	175.5(9)°	N150	Ni1	N13	170.9(5)°
N14	Ni1	N13	80.6(3)°	S1	Ni1	N160	88.1(8)°
N150	Ni1	N160	100.0(4)°	N14	Ni1	N160	169.0(4)°
S1	Ni1	N16	86.5(7)°	S4 1_455	Ni1	N16	93.8(7)°
N15	Ni1	N16	97.7(4)°	N150	Ni1	N16	108.3(3)°
N14	Ni1	N16	160.8(4)°	N140	Ni1	N130	79.0(3)°
N140	Ni1	N13	71.4(4)°	N130	Ni1	N13	7.7(4)°
N140	Ni1	N160	160.1(4)°	N130	Ni1	N160	81.1(3)°
N13	Ni1	N160	88.7(3)°	N140	Ni1	N16	151.7(3)°
N130	Ni1	N16	72.7(4)°	N13	Ni1	N16	80.3(3)°
N160	Ni1	N16	8.5(4)°	S2	Ni2	S7	169.68(9)°
S2	Ni2	N18	83.8(6)°	S7	Ni2	N18	85.9(6)°
S2	Ni2	N180	85.8(6)°	S7	Ni2	N180	84.0(6)°
N18	Ni2	N180	10.7(4)°	S2	Ni2	N170	89.2(9)°
S7	Ni2	N170	87.5(8)°	N18	Ni2	N170	70.8(4)°
N180	Ni2	N170	81.4(3)°	S2	Ni2	N17	89.0(0)°
S7	Ni2	N17	88.8(9)°	N18	Ni2	N17	77.0(3)°
N180	Ni2	N17	87.6(3)°	N170	Ni2	N17	6.2(4)°
S2	Ni2	N200	95.8(8)°	S7	Ni2	N200	93.3(8)°
N18	Ni2	N200	151.0(3)°	N180	Ni2	N200	161.4(4)°
N170	Ni2	N200	80.1(3)°	S2	Ni2	N20	95.6(9)°
S7	Ni2	N20	94.0(9)°	N18	Ni2	N20	157.6(4)°
N180	Ni2	N20	168.0(4)°	N170	Ni2	N20	86.7(4)°
S2	Ni2	N19	91.5(6)°	S7	Ni2	N19	90.8(6)°
N18	Ni2	N19	98.9(4)°	N180	Ni2	N19	88.3(4)°
N170	Ni2	N19	169.4(4)°	S2	Ni2	N190	88.0(5)°
S7	Ni2	N190	95.4(5)°	N2	C2	S2	176.6(8)°
N22	Ni3	N24	164.6(3)°	N4	C4	S4	176.1(8)°
N21	Ni3	S8	88.6(2)°	N6	C6	S6	178.4(8)°
N23	Ni3	S8	92.4(3)°	N8	C8	S8	177.1(8)°
N1	C1	S1	178.9(8)°	N10	C10	S10	176.8(9)°
N11	C11	S11	178.8(9)°				

Figure S4. Detail of the layer packing for compound **1**. Only the metal ions connected by NCS ligands are depicted. The shortest separations between metal ions from different layers are 8.30 Å for Ni2-Ni3*(2-x, 1-y, 2-z)* and 8.61 Å for Mo2-Mo2*(2-x, 1-y, 2-z)*

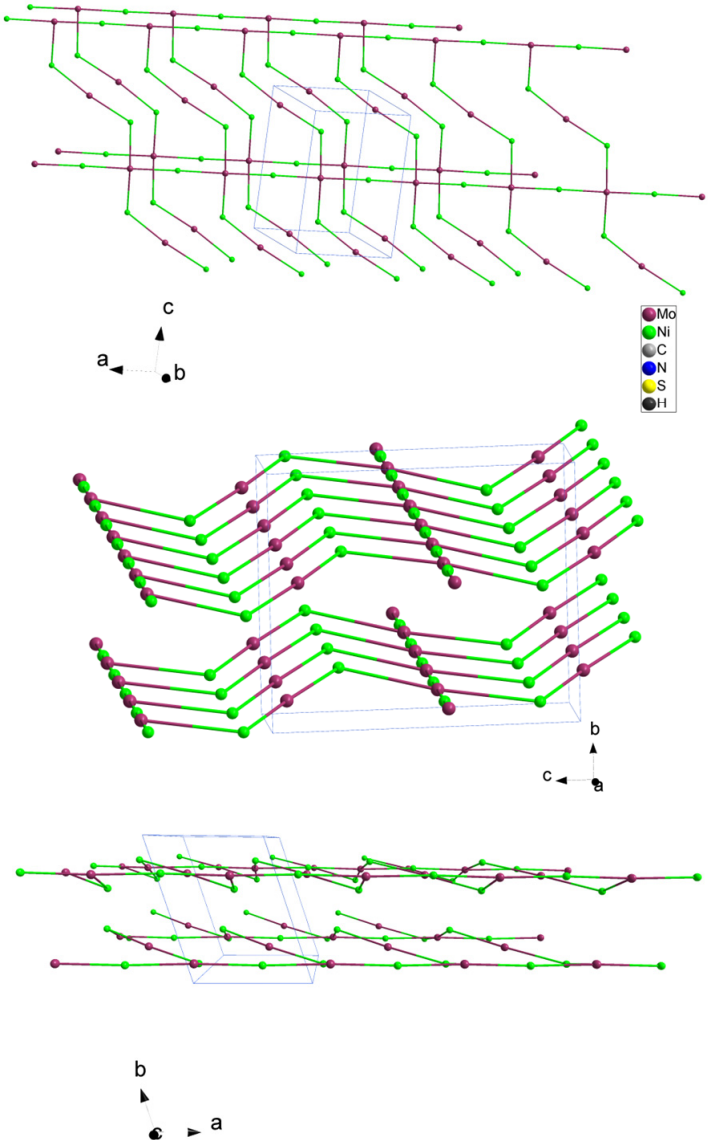


Figure S5. Powder X-ray diffraction pattern for **1** and **2**. Experimental diffractograms of **1** (red) and **2** (blue), and simulated powder pattern from structure data of **1** (black).

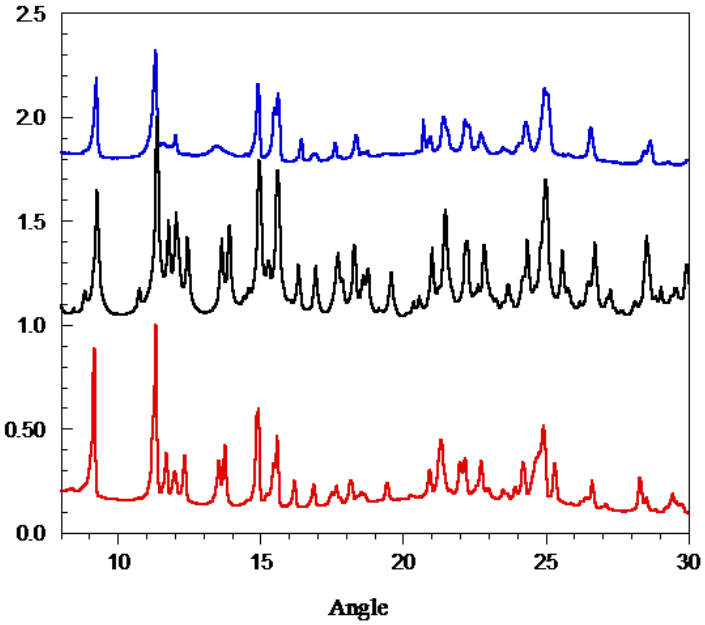
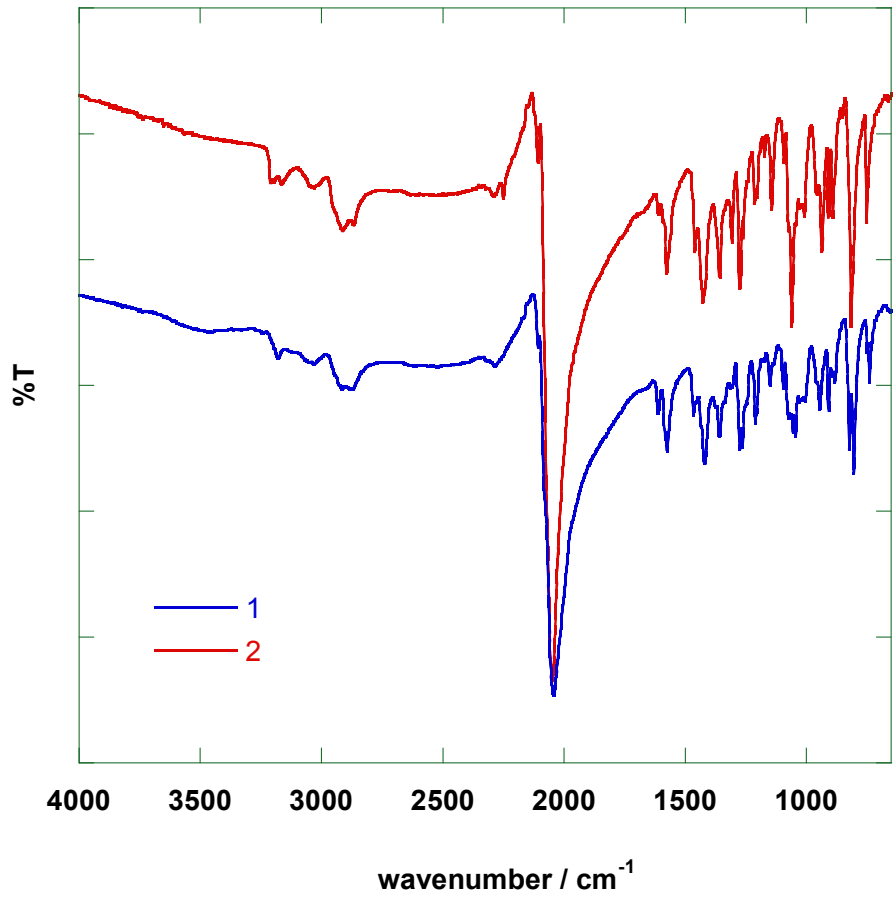


Figure S6. IR spectra for **1** and **2**.



FT-IR (ATR) main bands, ν (cm^{-1}):

1: 3179 (w), 3030 (w), 2914 (w), 2106 (w), 2042 (s), 1574 (m), 1419 (m), 1359 (m), 1312 (w), 1274 (m), 1263 (m), 1210 (m), 1149 (w), 1095 (w), 1056 (m), 1044 (m), 945 (m), 908 (m), 823 (m), 804 (m), 749 (w), 739 (m), 641 (w).

2: 3162 (w), 3036 (w), 2912 (w), 2107 (w), 2050 (s), 1576 (m), 1460 (w), 1426 (m), 1357 (m), 1307 (w), 1274 (m), 1260 (w), 1142 (w), 1092 (w), 1060 (m), 936 (m), 909 (m), 815 (m), 751 (m).

Figure S7. *M* versus *H* behavior for **1** at 2 K.

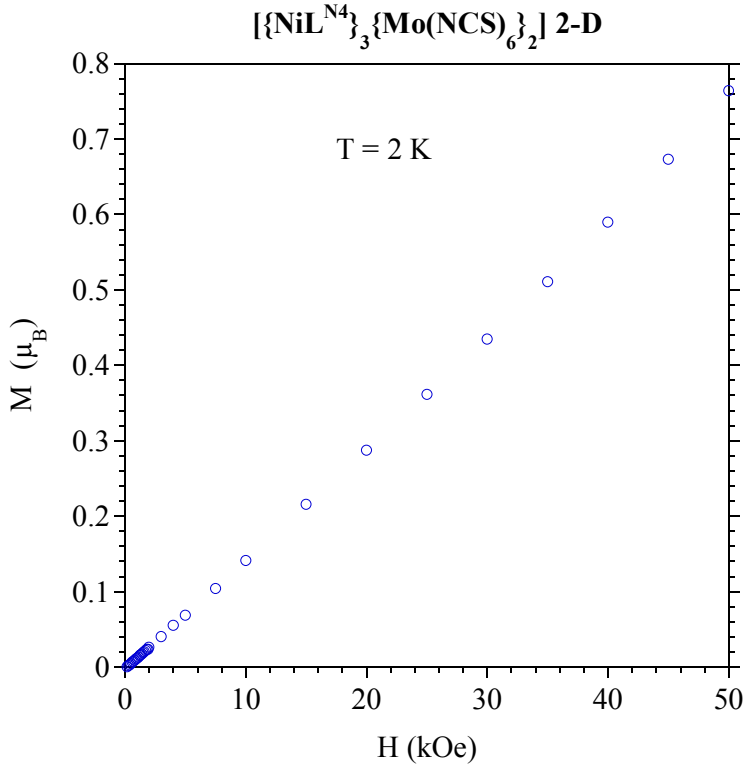


Figure S8. *M* versus *H* hysteresis loops for **2**.