Electronic Supplementary Information (ESI)

Figure S1. IR spectra of 1-MeIm (liquid) and complexes **1** and **2** in solid state.

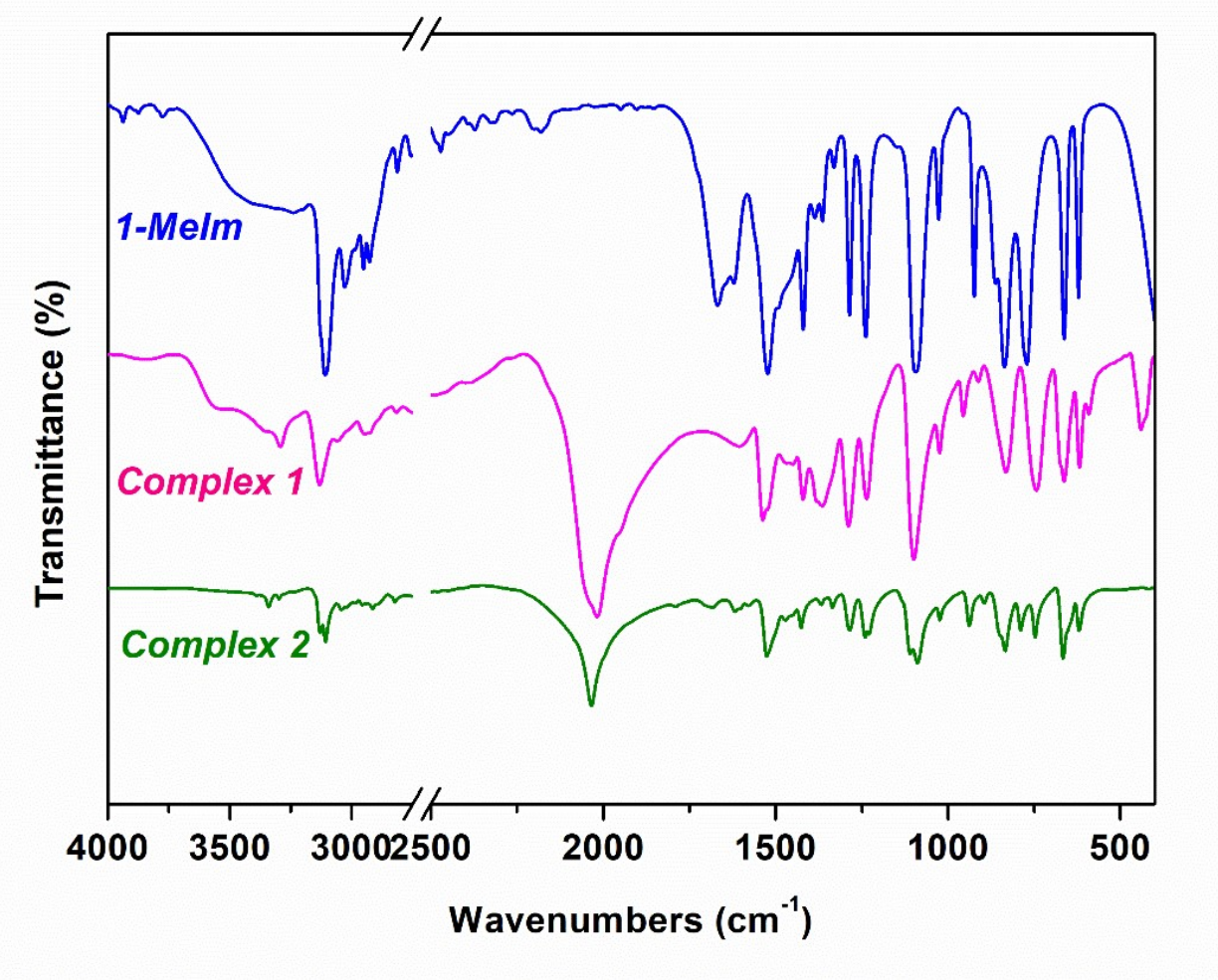


Figure S2. Raman spectra of 1-MeIm (liquid) and complexes **1** and **2** in solid state.

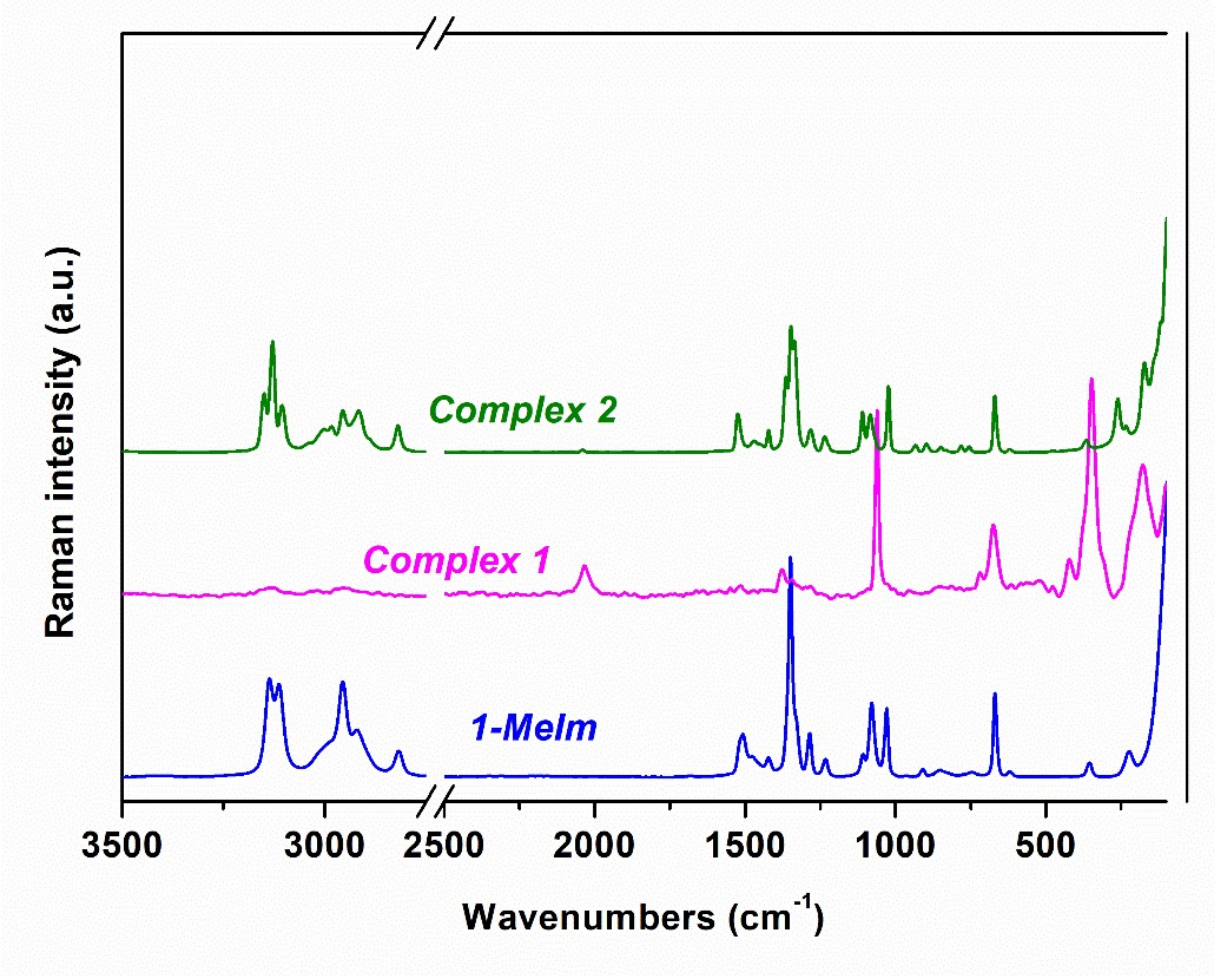


Figure S3. Electronic spectra (in acetonitrile) of complexes **1** and **2**.

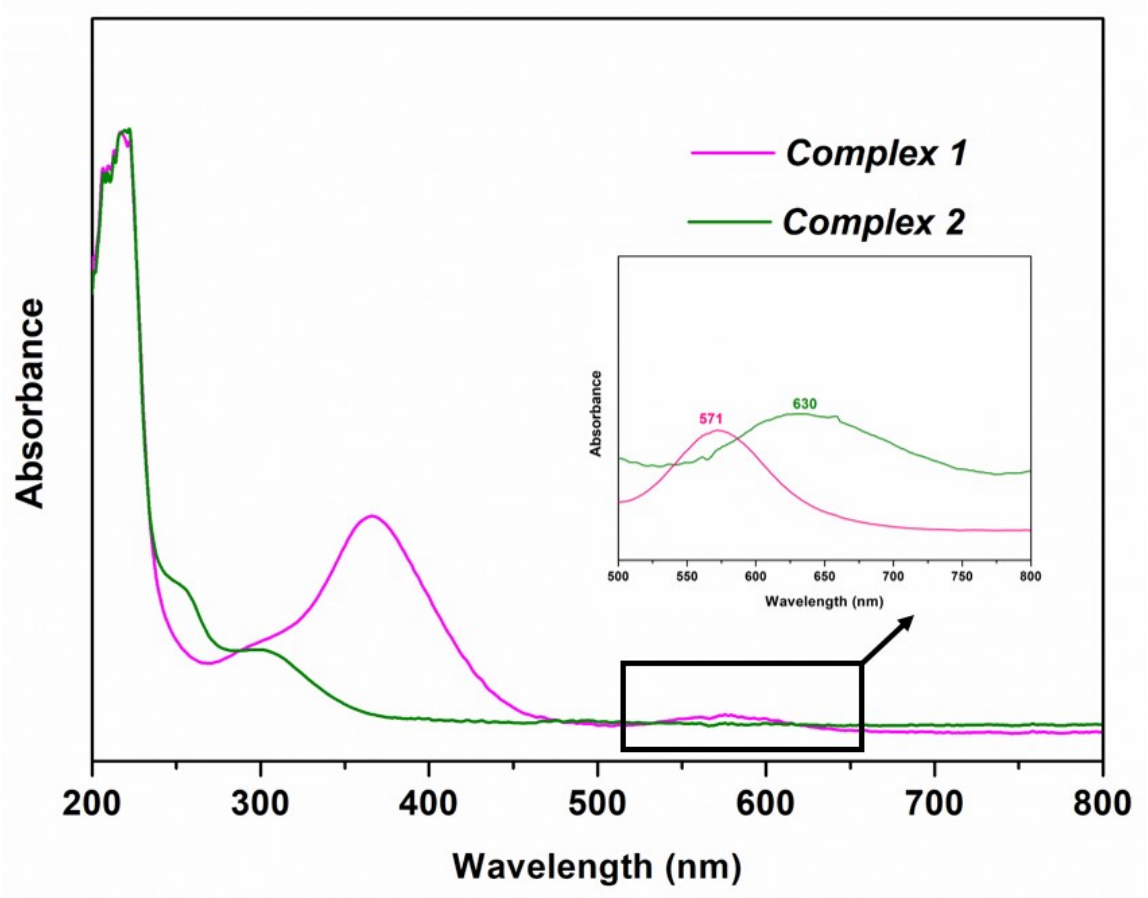


Figure S4. The temperature dependence for the effective magnetic moment (μ_{eff}).

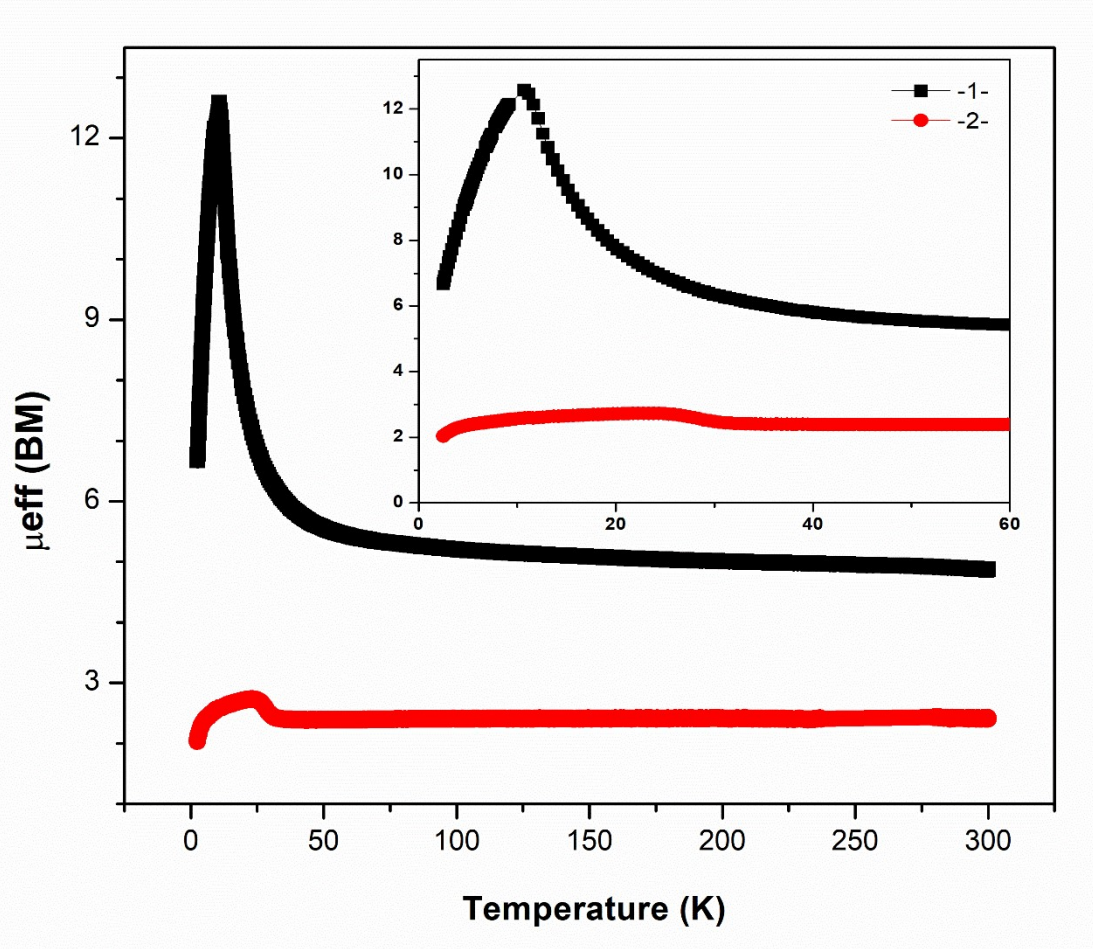


Figure S5. Plots of χ^{-1} versus T for complexes **1** and **2**. Solid line is the best fit to the Curie-Weiss law.

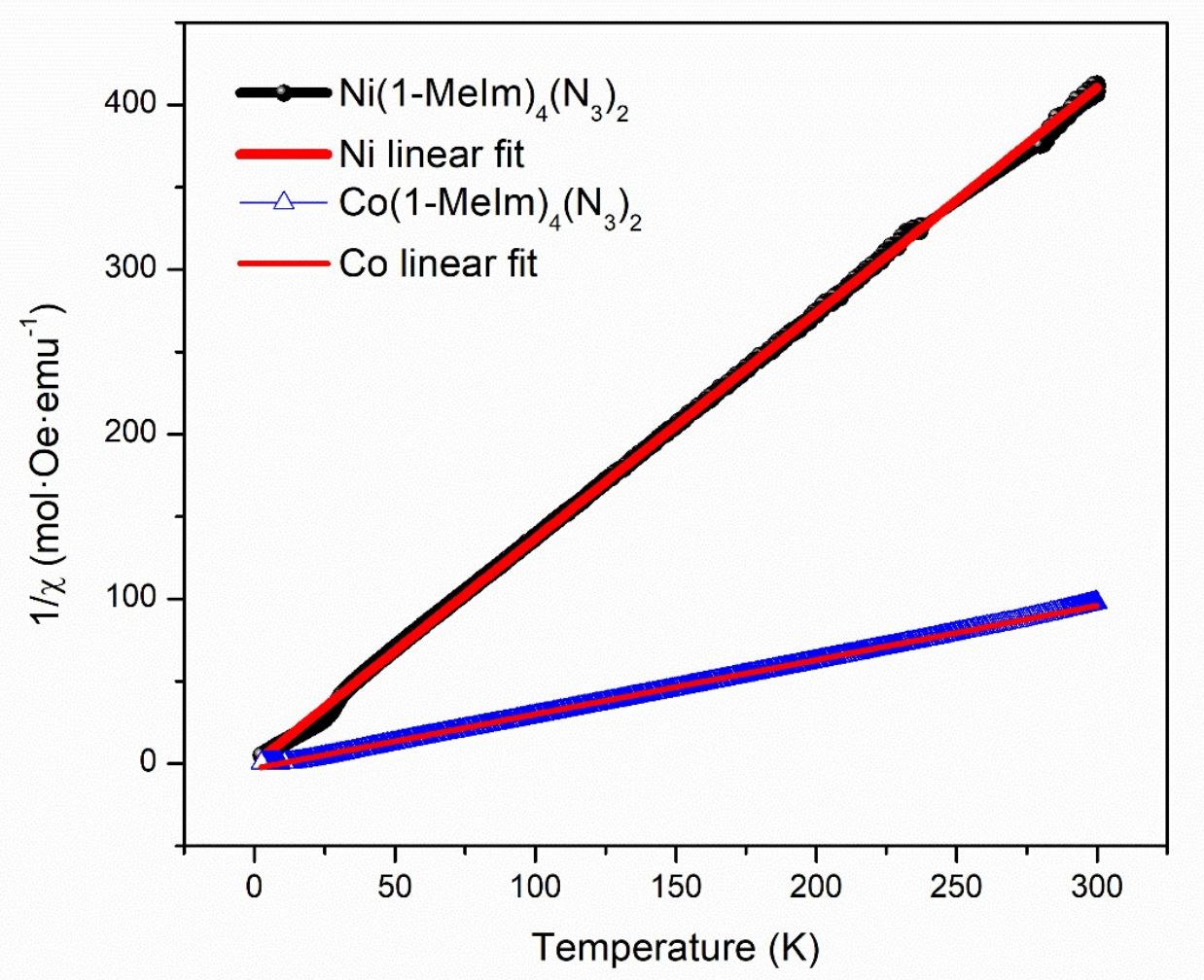
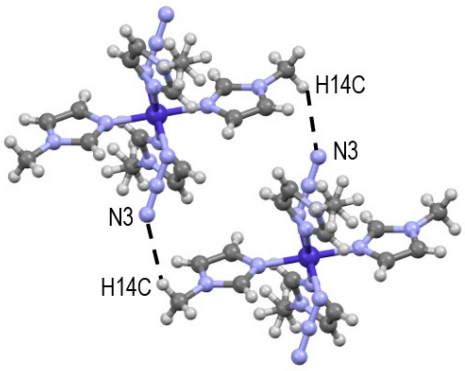
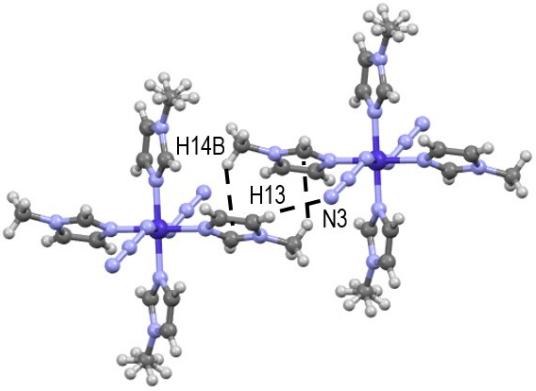


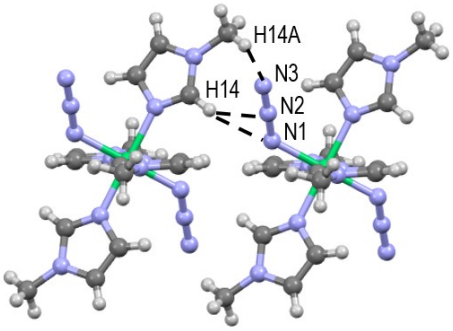
Figure S6. Types of H-bonded dimers extracted from the crystal structures of **1** (**Ia** and **Ib**) and **2** (**IIa** and **IIb**) and used for DFT calculations.



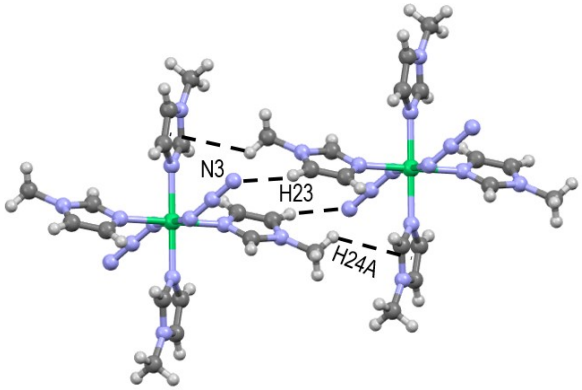
Ia – d(Co···Co) = 7.909 Å



Ib – d(Co···Co) = 9.172 Å



IIa – d(Ni···Ni) = 6.917 Å



IIb – d(Ni···Ni) = 9.275 Å

Figure S7. In -phase χ' and out-of-phase χ''susceptibilities for complex **2**, no frequency dependence is observed.

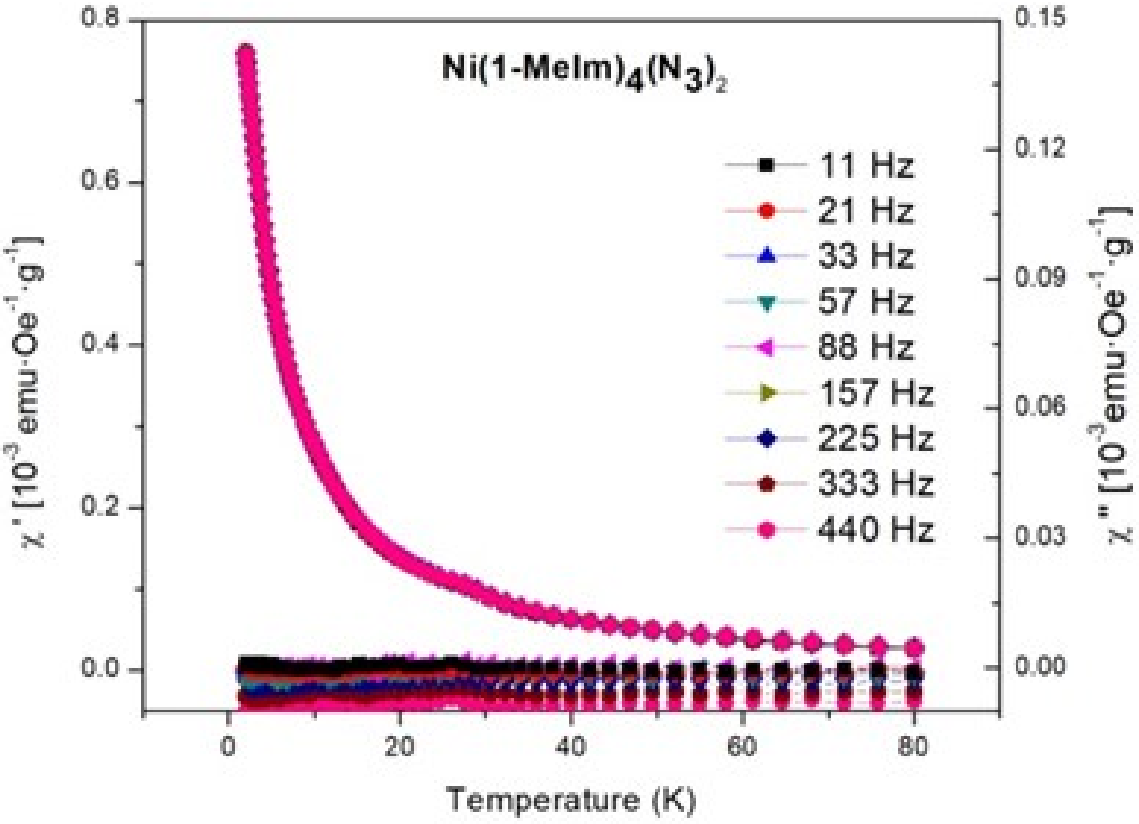


Figure S8. Magnetization versus Magnetic field measurements for complex **1** at different temperatures. Zoom in: non-null coercivity is evidenced below 15 K.

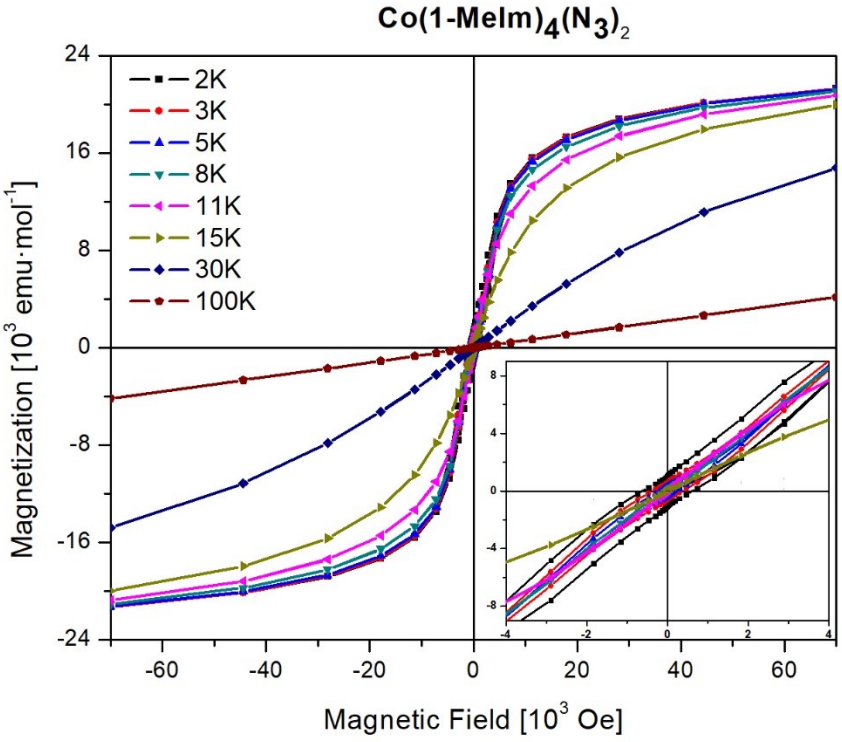


Table S1a. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Co(1\text{-}MeIm)_4(N_3)_2]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(11)	6312(3)	3800(3)	7788(3)	32(1)
C(12)	6786(4)	6036(3)	7093(3)	39(1)
C(13)	7423(4)	5553(4)	8358(3)	43(1)
C(14)	7616(4)	3166(4)	10112(3)	49(1)
C(21)	3005(4)	8061(3)	6186(3)	39(1)
C(22)	1153(3)	6829(4)	5947(4)	45(1)
C(23)	162(4)	8195(4)	6502(4)	50(1)
C(24)	885(5)	10522(4)	7261(5)	74(1)
N(1)	6263(3)	6540(2)	4018(2)	36(1)
N(2)	7242(3)	6381(2)	2806(3)	35(1)
N(3)	8184(4)	6319(3)	1646(3)	63(1)
N(11)	6070(2)	4927(2)	6736(2)	30(1)
N(12)	7129(3)	4131(3)	8796(2)	36(1)
N(21)	2951(2)	6736(2)	5749(2)	30(1)
N(22)	1344(3)	8982(3)	6653(3)	42(1)
Co	50005000	500027(1)		

Table S1b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ni(1\text{-}MeIm)_4(N_3)_2]$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(11)	1829(4)	7653(3)	8863(3)	30(1)
C(12)	4437(4)	8514(3)	9037(3)	42(1)
C(13)	3255(4)	9723(3)	8461(3)	48(1)
C(14)	-96(6)	10060(4)	7715(5)	56(1)
C(21)	5935(4)	3620(3)	7134(3)	34(1)
C(22)	2748(4)	4153(3)	7798(3)	32(1)
C(23)	3106(4)	3543(3)	6540(3)	35(1)
C(24)	6233(6)	2416(5)	4898(4)	55(1)
N(1)	7838(3)	5673(3)	8725(2)	38(1)
N(2)	8182(3)	6408(3)	7478(3)	37(1)
N(3)	8573(4)	7147(4)	6266(3)	69(1)
N(11)	3548(3)	7209(2)	9292(2)	30(1)
N(12)	1592(3)	9173(2)	8340(2)	36(1)
N(21)	4538(3)	4212(2)	8170(2)	29(1)
N(22)	5149(3)	3193(2)	6134(2)	33(1)
Ni	50005000	1000027(1)		

Table S2a. Full bond lengths [Å] and angles [°] for $[Co(1\text{-}MeIm)_4(N_3)_2]$.

C(11)-N(11)	1.318(3)	N(3)-N(2)-N(1)	175.9(3)
C(11)-N(12)	1.343(3)	C(11)-N(11)-C(12)	105.6(2)
C(12)-C(13)	1.345(4)	C(11)-N(11)-Co	127.58(17)
C(12)-N(11)	1.383(3)	C(12)-N(11)-Co	126.81(19)
C(13)-N(12)	1.367(4)	C(11)-N(12)-C(13)	106.9(2)
C(14)-N(12)	1.460(3)	C(11)-N(12)-C(14)	127.0(2)
C(21)-N(21)	1.315(3)	C(13)-N(12)-C(14)	126.1(2)
C(21)-N(22)	1.338(3)	C(21)-N(21)-C(22)	105.4(2)
C(22)-C(23)	1.336(4)	C(21)-N(21)-Co	127.16(17)
C(22)-N(21)	1.371(3)	C(22)-N(21)-Co	127.40(18)
C(23)-N(22)	1.365(4)	C(21)-N(22)-C(23)	106.9(2)
C(24)-N(22)	1.468(4)	C(21)-N(22)-C(24)	126.4(2)
N(1)-N(2)	1.201(3)	C(23)-N(22)-C(24)	126.7(2)
N(1)-Co	1.961(2)	N(11)-Co-N(11)#1	180.0
N(2)-N(3)	1.150(3)	N(11)-Co-N(21)#1	88.06(8)
N(11)-Co	1.9504(19)	N(11)#1-Co-N(21)#1	91.94(8)
N(21)-Co	1.9510(18)	N(11)-Co-N(21)	91.94(8)
Co-N(11)#1	1.9504(19)	N(11)#1-Co-N(21)	88.06(8)
Co-N(21)#1	1.9510(18)	N(21)#1-Co-N(21)	180.0
Co-N(1)#1	1.961(2)	N(11)-Co-N(1)	88.64(9)
		N(11)#1-Co-N(1)	91.36(9)
N(11)-C(11)-N(12)	111.3(2)	N(21)#1-Co-N(1)	92.33(8)
C(13)-C(12)-N(11)	109.1(3)	N(21)-Co-N(1)	87.67(8)
C(12)-C(13)-N(12)	107.0(2)	N(11)-Co-N(1)#1	91.36(9)
N(21)-C(21)-N(22)	111.3(2)	N(11)#1-Co-N(1)#1	88.64(9)
C(23)-C(22)-N(21)	109.7(3)	N(21)#1-Co-N(1)#1	87.67(8)
C(22)-C(23)-N(22)	106.8(2)	N(21)-Co-N(1)#1	92.33(8)
N(2)-N(1)-Co	122.94(16)	N(1)-Co-N(1)#1	180.0

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

Table S2b. Bond lengths [Å] and angles [°] for $[Ni(1\text{-}MeIm)_4(N_3)_2]$.

C(11)-N(11)	1.317(3)	N(11)#1-Ni-N(1)	89.11(8)
C(11)-N(12)	1.348(3)	N(11)-Ni-N(1)	90.89(8)
C(12)-C(13)	1.342(4)	N(1)#1-Ni-N(1)	180.0
C(12)-N(11)	1.371(3)		
C(13)-N(12)	1.367(4)		
C(14)-N(12)	1.467(4)		
C(21)-N(21)	1.318(3)		
C(21)-N(22)	1.339(3)		
C(22)-C(23)	1.353(4)		
C(22)-N(21)	1.378(3)		
C(23)-N(22)	1.369(3)		
C(24)-N(22)	1.460(4)		
N(1)-N(2)	1.184(3)		
N(1)-Ni	2.129(2)		
N(2)-N(3)	1.162(3)		
N(11)-Ni	2.1196(18)		
N(21)-Ni	2.0969(19)		
Ni-N(21)#1	2.0970(19)		
Ni-N(11)#1	2.1196(18)		
Ni-N(1)#1	2.129(2)		
N(11)-C(11)-N(12)	111.2(2)		
C(13)-C(12)-N(11)	110.0(3)		
C(12)-C(13)-N(12)	106.5(2)		
N(21)-C(21)-N(22)	112.1(2)		
C(23)-C(22)-N(21)	110.0(2)		
C(22)-C(23)-N(22)	106.0(2)		
N(2)-N(1)-Ni	126.68(17)		
N(3)-N(2)-N(1)	177.7(3)		
C(11)-N(11)-C(12)	105.4(2)		
C(11)-N(11)-Ni	131.24(17)		
C(12)-N(11)-Ni	123.01(17)		
C(11)-N(12)-C(13)	106.8(2)		
C(11)-N(12)-C(14)	126.6(3)		
C(13)-N(12)-C(14)	126.6(3)		
C(21)-N(21)-C(22)	104.8(2)		
C(21)-N(21)-Ni	126.58(17)		
C(22)-N(21)-Ni	128.64(17)		
C(21)-N(22)-C(23)	107.1(2)		
C(21)-N(22)-C(24)	127.0(3)		
C(23)-N(22)-C(24)	125.8(3)		
N(21)-Ni-N(21)#1	180.0		
N(21)-Ni-N(11)#1	87.83(7)		
N(21)#1-Ni-N(11)#1	92.17(7)		
N(21)-Ni-N(11)	92.17(7)		
N(21)#1-Ni-N(11)	87.83(7)		
N(11)#1-Ni-N(11)	180.00(10)		
N(21)-Ni-N(1)#1	88.55(8)		
N(21)#1-Ni-N(1)#1	91.45(8)		
N(11)#1-Ni-N(1)#1	90.89(8)		
N(11)-Ni-N(1)#1	89.11(8)		
N(21)-Ni-N(1)	91.45(8)		
N(21)#1-Ni-N(1)	88.55(8)		

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

Table S3a. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Co(1\text{-}MeIm)_4(N_3)_2]$. The anisotropic
displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(11)	33(1)	31(2)	32(1)	-5(1)	-3(1)	-9(1)
C(12)	46(2)	35(2)	43(2)	1(1)	-16(1)	-18(1)
C(13)	49(2)	45(2)	44(2)	-4(1)	-19(1)	-19(1)
C(14)	54(2)	56(2)	35(2)	5(1)	-15(1)	-11(2)
C(21)	35(1)	35(2)	48(2)	-11(1)	-7(1)	-7(1)
C(22)	33(1)	37(2)	66(2)	-8(2)	-8(1)	-8(1)
C(23)	34(2)	42(2)	65(2)	-8(2)	-4(1)	2(1)
C(24)	77(2)	47(2)	92(3)	-35(2)	-27(2)	8(2)
N(1)	44(1)	32(1)	33(1)	-6(1)	1(1)	-18(1)
N(2)	37(1)	32(1)	40(1)	-2(1)	-6(1)	-15(1)
N(3)	66(2)	72(2)	47(2)	-12(2)	15(1)	-33(2)
N(11)	31(1)	29(1)	30(1)	-5(1)	-5(1)	-9(1)
N(12)	35(1)	44(1)	28(1)	0(1)	-9(1)	-8(1)
N(21)	31(1)	28(1)	30(1)	-3(1)	-4(1)	-7(1)
N(22)	45(1)	30(1)	47(2)	-12(1)	-10(1)	1(1)
Co	30(1)	26(1)	26(1)	-3(1)	-4(1)	-9(1)

Table S3b. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Ni(1\text{-}MeIm)_4(N_3)_2]$. The anisotropic
displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(11)	30(1)	27(1)	36(1)	-8(1)	-10(1)	-2(1)
C(12)	35(2)	32(1)	60(2)	-5(1)	-16(1)	-8(1)
C(13)	48(2)	29(2)	65(2)	-5(2)	-10(2)	-8(1)
C(14)	55(2)	45(2)	71(2)	-6(2)	-34(2)	12(2)
C(21)	29(2)	37(1)	36(1)	-9(1)	-8(1)	-3(1)
C(22)	29(1)	30(1)	38(1)	-5(1)	-11(1)	1(1)
C(23)	39(2)	32(1)	37(1)	-3(1)	-20(1)	-3(1)
C(24)	65(2)	61(2)	39(2)	-22(2)	0(2)	-9(2)
N(1)	25(1)	50(1)	39(1)	-5(1)	-7(1)	-7(1)
N(2)	26(1)	52(1)	40(1)	-15(1)	-8(1)	-12(1)
N(3)	73(2)	98(2)	39(1)	4(2)	-14(1)	-40(2)
N(11)	29(1)	26(1)	33(1)	-5(1)	-10(1)	-1(1)
N(12)	35(1)	29(1)	42(1)	-4(1)	-12(1)	2(1)
N(21)	28(1)	30(1)	31(1)	-7(1)	-12(1)	1(1)
N(22)	39(1)	32(1)	27(1)	-6(1)	-6(1)	-5(1)
Ni	23(1)	29(1)	30(1)	-7(1)	-9(1)	-1(1)

Table S4a. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $[Co(1\text{-MeIm})_4(N_3)_2]$.

Atom	x	y	z	U(eq)
H(14A)	72842215	1015373		
H(14B)	69913716	1099973		
H(14C)	88952931	1004873		
H(24A)	-40310932	7510110		
H(24B)	137510431	8145110		
H(24C)	138311211	6526110		
H(24D)	197310784	7277110		
H(24E)	19511285	6642110		
H(24F)	18710505	8262110		
H(11)	5970(30)	2880(30)	7880(30)	28(6)
H(12)	6760(30)	7000(30)	6470(30)	41(7)
H(13)	7910(40)	6030(40)	8920(40)	58(9)
H(21)	4040(40)	8340(30)	6210(30)	45(8)
H(22)	800(30)	5890(40)	5700(30)	49(8)
H(23)	-1070(40)	8750(40)	6670(40)	62(9)

Table S4b. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å x 10^3) for $[Ni(1\text{-MeIm})_4(N_3)_2]$.

Atom	x	y	z	U(eq)
H(12)	5700(40)	8470(30)	9320(30)	42(7)
H(13)	3410(40)	10760(30)	8220(30)	52(8)
H(14)	880(30)	7020(30)	8890(20)	28(6)
H(14A)	-870(60)	9430(40)	7490(40)	87(13)
H(14B)	370(60)	10650(40)	6740(40)	100(14)
H(14C)	-810(50)	10790(50)	8320(40)	93(13)
H(21)	7300(40)	3490(30)	7070(20)	30(7)
H(22)	1450(40)	4500(30)	8390(30)	49(8)
H(23)	2230(40)	3420(30)	5940(30)	58(9)
H(24A)	5720(50)	2820(40)	4050(40)	84(12)
H(24B)	6300(60)	1380(50)	5200(40)	105(15)
H(24C)	7700(60)	2630(40)	4670(40)	97(13)