Supplementary Material (ESI) for Chemical Communications

The coordination preferences of metal centres modulate superexchange coupling interactions in a metallo-supramolecular helical assembly

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Electronic Supplementary Information (ESI)

Physical measurements and experimental techniques

Materials

All solvents, 2,6-diacetylpyridine, 4-methoxybenzylcarbazate and tetraethylammonium perchlorate are commercially available and were used without further purification. Copper and nickel metals (Ega Chemie) were used as ca. 2 × 2 cm^2 plates.

Physical Measurements

Elemental analysis of C, H, N and S was performed on a FISONS EA 1108 analyzer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-500 spectrometer, using DMSO-d_6 as solvent. Fast atom bombardment mass spectra (FAB) were obtained on a Kratos MS-50 mass spectrometer, employing Xe atoms at 70 KeV in m-nitrobenzyl alcohol as a matrix; electrospray ionization mass spectra (ESI+) were recorded on an API4000 Applied Biosystems mass spectrometer with Triple Quadrupole analyzer. Conductivity was measured at 25 ºC from 10^{-3} M solutions in DMF on a Crison micro CM 2200 conductivimeter. Magnetic measurements were performed at variable temperatures (2–300 K) and variable applied magnetic field (0–6 T) using a Cryogenic S600 SQUID magnetometer. Raw data were corrected for the sample holder contribution, measured in the same temperature range, and the intrinsic diamagnetism of the samples, estimated by Pascal's constant.

Synthesis of H_2L

H_2L (Chart S1) was prepared by condensation of 4-methoxybenzylcarbazate (0.57 g, 4.8 mmol) with 2,6-diacetylpyridine (0.46 mL, 4.8 mmol) in ethanol (150 cm^3). The solution was heated under reflux for 5 h, concentrated with a Dean–Stark trap to ca. 30 cm^3 and cooled for 12 h (4 ºC). The white precipitate was filtered off, washed with diethyl ether (3 × 10 mL) and dried *in vacuo*.

H_2L: Yield 85%; m.p. = 200–201 ºC; E.A. (Found: C, 62.2; H, 5.7; N, 13.4; $C_{27}H_{29}N_5O_6$ required: C, 62.0; H, 5.6; N, 13.5); FAB base peak: 520.2 amu (H_2L + H, 100%); IR (KBr, cm^{-1}): ν(NH) 3243, 3158, ν(Amide I) 1711, ν(C=N)+ν(C–N) 1613, ν(Amide II) 1569, ν(N–N) 1032; ^{1}H NMR (DMSO-d_6, ppm): 10.41 (s, 2H); 7.95 (d, 2H, J = 7.2 Hz), 7.84 (t, 1H, J = 7.2 Hz); 7.38 (d, 4H, J = 8.5 Hz); 6,95 (d, 4H, J = 8.5 Hz); 5.14 (s, 4H); 3.75 (s, 6H); 2.32 (s, 6H). ^{13}C NMR (DMSO-d_6, ppm): δ 159.1 (C=O), 153.9 (C=N), 153.0 (CN_{py}), 130.2, 129.7, 128.1, 113.8, 113.4 (C_{ar}), 54.9 (CH_2), 30.7 (CH_3O).12.9 (CH_{3Ac}).

General procedure for preparation of the complexes

The complexes $[Cu^{II}_2(\mathbf{L})_2]$ and $[Ni^{II}_2(\mathbf{L})_2]$ were synthesized by an electrochemical method[1] improved by us.[2] The general procedure can be typified as follows:
An acetonitrile solution of the ligand H_2L containing *ca.* 10 mg of tetraethylammonium perchlorate, as supporting electrolyte, was electrolyzed using a platinum wire as the cathode and a metal plate as the anode. The cell can be summarized as: Pt(–)|H_2L + CH_3CN|M(+), where M = Ni, Cu. (*Caution! Although problems were not encountered in our experiments, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care*). The resulting solids were filtered off, washed with diethyl ether and dried *in vacuo*.

$[Cu^{II}_2(\mathbf{L})_2]$: Yield 89%; m.p.>300 ºC; E.A. (Found: C, 55.7; H, 4.7; N, 11.9; $C_{54}Cu_2H_{54}N_{10}O_{12}$ required: C, 55.8; H, 4.7; N, 12.0); ESI-MS (*m*/*z*) 581.3 $[CuL]^+$; 1163.3, $[Cu_2L_2 + H]^+$; IR (KBr, cm^{-1}): ν(Amide I)+ ν(C=N) 1715, ν(Amide II) 1514, ν(N–N) 1031; Λ_M = 5.2 μS cm^{-1}. Slow evaporation of an acetonitrile solution of the precipitated obtained yielded brown crystals of $[Cu^{II}_2(\mathbf{L})_2]\cdot 2H_2O$ (**1**), which was characterized by X-ray diffraction.

$[Ni^{II}_2(\mathbf{L})_2]$: Yield 71%; m.p. >300 ºC; E.A. (Found: C, 56.3; H, 4.8; N, 12.0; $C_{54}H_{54}N_{10}Ni_2O_{12}$ required: C, 56.3; H, 4.7; N, 12.1); ESI-MS (*m*/*z*) 576.2 $[NiL]^+$, 1153.3 $[Ni_2L_2 + H]^+$; IR (KBr, cm^{-1}): ν(Amide I)+ ν(C=N) 1706, ν(Amide II) 1513, ν(N–N) 1023; Λ_M = 7.4 μS cm^{-1}. Slow evaporation of the mother liquors yielded the crystalline complex $[Ni^{II}_2(\mathbf{L})_2]$ **2**, which was characterized by X-ray diffraction.

Crystal Structure Determinations

Colourless needles and prismatic crystals of **1** and **2**, respectively, were mounted on a glass fibre and used for data collection. Crystal data were collected at 293(2) K for **1** and 100(2) K for **2**, using a Smart-CCD-1000 BRUKER diffractometer. Graphite monochromated MoK(α) radiation (λ = 0.71073 Å) was used throughout. The data were processed with BRUKER SAINT[3] and corrected for absorption using SADABS.[4] The structure was solved by SIR-97 [5] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97.[6] Positional and anisotropic atomic displacement parameters were refined for all heteroatoms. Hydrogen atoms bonded to carbon were placed geometrically and the H_2O hydrogen atoms were initially positioned at sited determined from difference maps, but the positional parameters for all H atoms were included as fixed contributions riding on attached atoms with isotropic thermal parameters (1.2–1.5) times those of their carrier atoms. Criteria for a satisfactory complete analysis were the ratios of "*rms*" shift to standard deviation less than 0.001 and no significant features in the final difference maps. Molecular graphics were prepared with Viewer Lab and ORTEP.[7] A highly disordered distribution of solvent for **2** was eliminated with SQUEEZE.[8] A summary of the crystal data, experimental details and refinement results are listed in Table S1. Significant bond distances and angles are summarized in Table S2 while hydrogen bond interactions parameters are listed in Table S3.

CCDC 767303 and 767304 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ww.ccdc.cam.ac.uk/data_request.cif.

Table S1. Selected bond lengths (Å) for helicates **1** and **2**

Bond lengths (Å)			
1		**2**	
C(1)–O(1)	1.44(2)	C(1)–O(1)	1.439(5)
C(2)–O(1)	1.369(14)	C(2)–O(1)	1.368(3)
C(8)–O(2)	1.470(11)	C(8)–O(2)	1.456(3)
C(11)–N(2)	1.296(11)	C(11)–N(2)	1.290(3)
C(12)–N(3)	1.356(10)	C(12)–N(3)	1.356(3)
C(16)–N(3)	1.332(11)	C(16)–N(3)	1.362(3)
C(18)–N(4)	1.291(10)	C(18)–N(4)	1.291(3)
C(19)–O(4)	1.250(10)	C(19)–O(4)	1.260(3)
C(19)–N(5)	1.340(11)	C(19)–N(5)	1.339(3)
C(19)–O(5)	1.353(10)	C(19)–O(5)	1.350(3)
C(20)–O(5)	1.466(11)	C(20)–O(5)	1.460(3)
C(24)–O(6)	1.377(13)	C(24)–O(6)	1.376(3)
C(27)–O(6)	1.404(15)	C(27)–O(6)	1.416(4)
C(28)–O(7)	1.424(13)	C(28)–O(7)	1.419(4)
C(29)–O(7)	1.362(11)	C(29)–O(7)	1.358(3)
C(35)–O(8)	1.447(10)	C(35)–O(8)	1.458(3)
C(36)–O(9)	1.267(10)	C(36)–O(9)	1.275(3)
C(36)–N(6)	1.333(11)	C(36)–N(6)	1.323(3)
C(36)–O(8)	1.337(10)	C(36)–O(8)	1.349(3)
C(38)–N(7)	1.279(10)	C(38)–N(7)	1.292(3)
C(39)–N(8)	1.340(10)	C(39)–N(8)	1.363(3)
C(43)–N(8)	1.375(11)	C(43)–N(8)	1.361(3)
C(45)–N(9)	1.274(11)	C(45)–N(9)	1.287(3)
C(54)–O(12)	1.427(14)	C(46)–O(10)	1.261(3)
N(2)–N(1)	1.389(10)	C(46)–N(10)	1.338(3)
N(2)–Cu(1)	1.930(7)	C(46)–O(11)	1.344(3)
N(3)–Cu(1)	2.184(6)	C(47)–O(11)	1.451(3)
N(4)–N(5)	1.386(9)	C(51)–O(12)	1.381(3)
N(4)–Cu(2)	1.946(7)	C(51)–C(52)	1.382(4)
N(6)–N(7)	1.372(10)	C(54)–O(12)	1.424(3)
N(7)–Cu(1)	1.971(7)	N(1)–N(2)	1.385(3)
N(8)–Cu(2)	2.228(6)	N(2)–Ni(1)	1.962(2)
N(9)–N(10)	1.35(2)	N(3)–Ni(1)	2.264(2)
N(9)–Cu(2)	1.906(8)	N(3)–Ni(2)	2.320(2)
O(4)–Cu(2)	2.128(6)	N(4)–N(5)	1.378(3)
O(9)–Cu(1)	2.204(6)	N(4)–Ni(2)	1.971(2)
O(12)–C(51)	1.367(11)	N(6)–N(7)	1.381(3)
Cu(2)–O(10)	2.04(2)	N(7)–Ni(1)	1.954(2)
Cu(1)–O(3)	2.003(6)	N(8)–Ni(2)	2.299(2)
N(1)–C(9)	1.323(9)	N(8)–Ni(1)	2.360(2)

C(9)–O(3)	1.262(9)	N(9)–N(10)	1.370(3)
C(9)–O(2)	1.349(9)	N(9)–Ni(2)	1.966(2)
N(10)–C(46)	1.338(15)	O(3)–Ni(1)	2.0381(17)
C(46)–O(10)	1.257(14)	O(4)–Ni(2)	2.0360(17)
C(46)–O(11)	1.350(14)	O(9)–Ni(1)	2.0468(18)
O(11)–C(47)	1.42(3)	O(10)–Ni(2)	2.0573(17)
Cu(2)–Cu(1)	3.2418(17)	Ni(1)–Ni(2)	3.0002(8)

Table S2. Selected bond angles (°) for helicates **1** and **2**

Angles (º)			
1		**2**	
O(3)–C(9)–O(2)	114.7(7)	O(3)–C(9)–O(2)	114.4(2)
N(1)–C(9)–O(2)	117.6(7)	N(1)–C(9)–O(2)	117.6(2)
C(11)–N(2)–N(1)	120.9(8)	C(11)–N(2)–N(1)	121.2(2)
N(3)–C(12)–C(11)	115.1(7)	N(3)–C(12)–C(11)	116.4(2)
N(3)–C(16)–C(15)	121.5(8)	N(3)–C(16)–C(15)	121.2(2)
C(18)–N(4)–N(5)	118.4(7)	C(18)–N(4)–N(5)	120.5(2)
N(5)–C(19)–O(5)	111.9(8)	N(5)–C(19)–O(5)	111.3(2)
O(4)–C(19)–N(5)	129.0(8)	O(4)–C(19)–N(5)	128.5(2)
N(9)–Cu(2)–O(10)	74.6(5)	N(9)–Ni(2)–O(10)	78.61(8)
N(9)–Cu(2)–N(8)	78.2(3)	N(9)–Ni(2)–N(8)	75.81(8)
N(4)–Cu(2)–O(4)	77.7(3)	N(8)–Ni(2)–N(3)	98.95(8)
O(4)–Cu(2)–O(10)	110.3(7)	N(4)–Ni(2)–N(3)	76.35(8)
N(9)–Cu(2)–N(4)	172.5(3)	N(4)–Ni(2)–O(4)	78.41(8)
O(9)–C(36)–O(8)	121.4(8)	O(4)–Ni(2)–O(10)	101.27(7)
O(9)–C(36)–N(6)	126.6(9)	N(9)–Ni(2)–N(4)	176.99(9)
C(38)–N(7)–N(6)	118.2(7)	O(9)–C(36)–O(8)	113.8(2)
N(8)–C(39)–C(38)	116.4(7)	O(9)–C(36)–N(6)	128.1(2)
N(8)–C(43)–C(45)	115.2(8)	C(38)–N(7)–N(6)	120.5(2)
C(45)–N(9)–N(10)	111.2(10)	N(8)–C(39)–C(38)	116.8(2)
O(10)–C(46)–N(10)	128.5(17)	N(8)–C(43)–C(45)	116.3(2)
O(10)–C(46)–O(11)	118.5(17)	C(45)–N(9)–N(10)	119.7(2)
N(7)–Cu(1)–O(3)	94.7(3)	O(10)–C(46)–N(10)	128.2(2)
N(2)–Cu(1)–N(3)	78.2(3)	O(10)–C(46)–O(11)	120.5(2)
N(2)–Cu(1)–O(3)	79.3(3)	N(7)–Ni(1)–O(3)	99.02(8)
O(3)–Cu(1)–O(9)	114.2(2)	N(7)–Ni(1)–N(8)	75.96(8)
N(7)–Cu(1)–N(2)	171.6(3)	N(2)–Ni(1)–N(3)	76.58(8)
		N(2)–Ni(1)–O(3)	78.95(8)
		O(3)–Ni(1)–O(9)	105.76(7)
		N(7)–Ni(1)–N(2)	175.37(9)
		N(3)–Ni(1)–N(8)	98.81(8)

Table S3. Hydrogen bond parameters [Å, °] for **1** and **2**

Parameter	D–H···A	D–H	H···A	D···A	∠DHA
		1			
	O13—H13B···N6	0.81 (6)	2.18 (7)	2.971 (11)	166 (13)
	O13—H13A···O12^{i}	0.87 (8)	2.19 (8)	3.027 (11)	163 (13)
	O14—H14B···O13^{ii}	0.94 (8)	2.04 (9)	2.979 (14)	177 (14)
	O14—H14A···N5^{ii}	0.84 (14)	2.25 (14)	3.047 (12)	159 (14)
	C10—H10C···N1	0.96	2.39	2.828 (12)	107
	C44—H44A···N10	0.96	2.17	2.60(2)	106
	C20—H20B···O1^{iii}	0.97	2.53	3.384(12)	147
	C26—H26···O4^{iv}	0.93	2.58	3.323(12)	137
	C27—H27A···O3^{v}	0.96	2.52	3.450(14)	162
	C42—H42···O7^{vi}	0.93	2.51	3.349(12)	151

Symmetry transformations: (i) $x+1, y+1, z$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $-x+1, -y, -z+1$; (v) $-x+1, -y+1, -z+1$; (vi) $x-1, y-1, z-1$

		2			
	C10—H10A ··· N1	0.96	2.44	2.851(3)	106
	C13—H13···O9^{i}	0.93	2.51	3.395(3)	159
	C17—H17A···N6	0.96	2.5	2.841(4)	101
	C26—H26···O4^{ii}	0.93	2.54	3.421(4)	159
	C27—H27C···O3^{iii}	0.96	2.39	3.299(4)	159
	C35—H35B···N7	0.97	2.23	2.668(4)	106
	C37—H37A···N7	0.96	2.5	2.838(4)	100
	C42—H42···O7^{iv}	0.93	2.37	3.264(4)	162

Symmetry transformations: (i) $-x+2, -y, -z+1$; (ii) $-x+2, -y+1, -z+2$; (iii) $-x+2, -y, -z+2$; (iv) $x+1, y+1, z+1$.

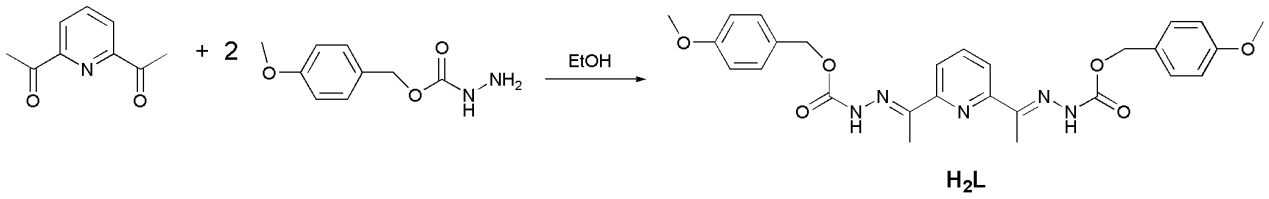

Chart S1: Synthesis of the ligand **H_2L**.

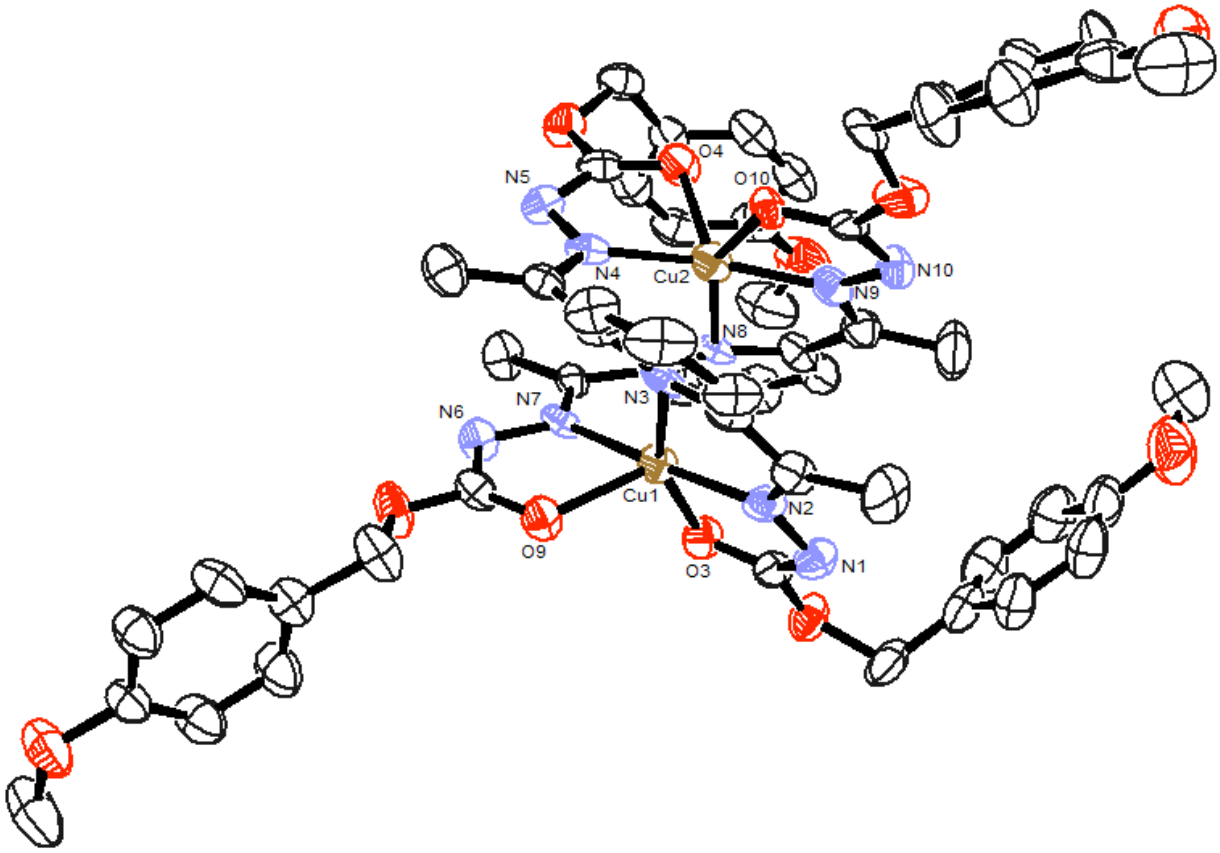

Figure S1. ORTEP diagram for the complex $[Cu^{II}_2(\mathbf{L})_2]\cdot 2H_2O$ **1**. Solvating water molecules and disordered atoms are not depicted for the sake of clarity.

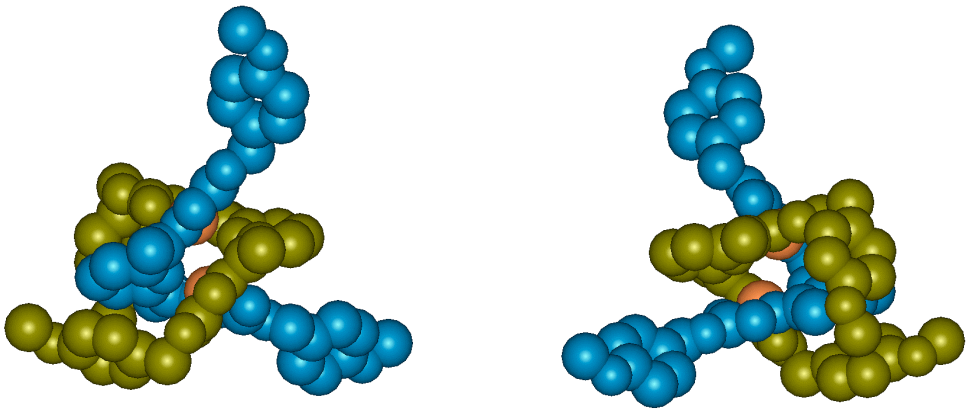

Figure S2. Major and minor grooves in the asymmetric helicate $[Cu^{II}_2(\mathbf{L})_2]\cdot 2H_2O$ **1**.

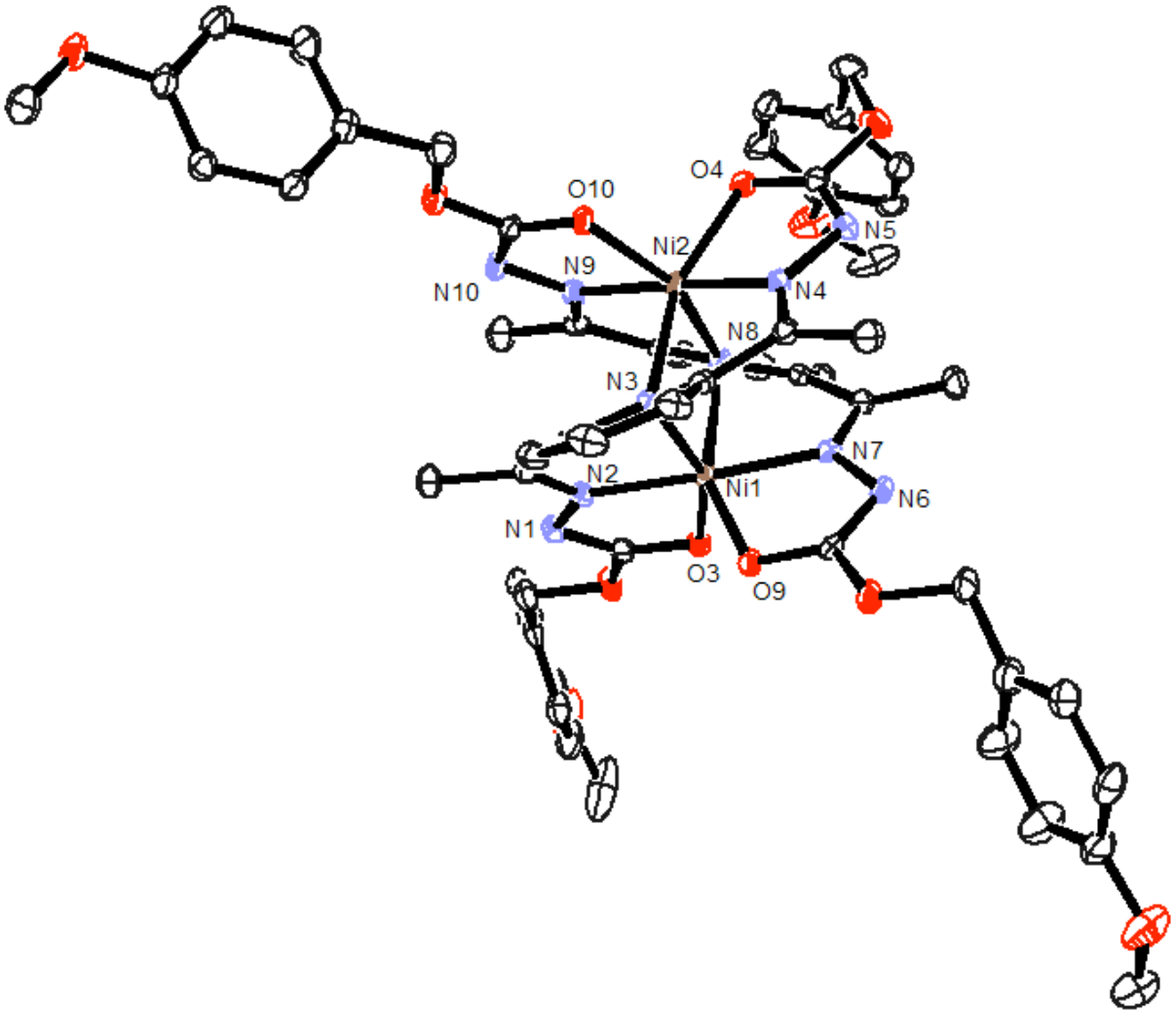

Figure S3. ORTEP diagram for the complex $[Ni^{II}_2(\mathbf{L})_2]$ (**2**).

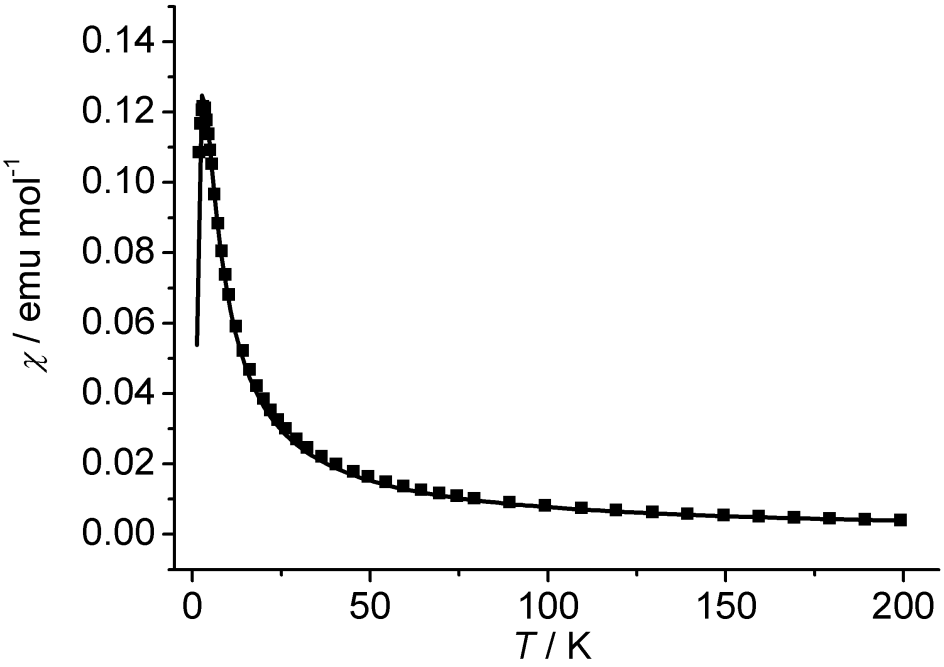

Figure S4. Plot of χ vs T curve for **1** and corresponding best fit curve obtained with parameters reported in the text.

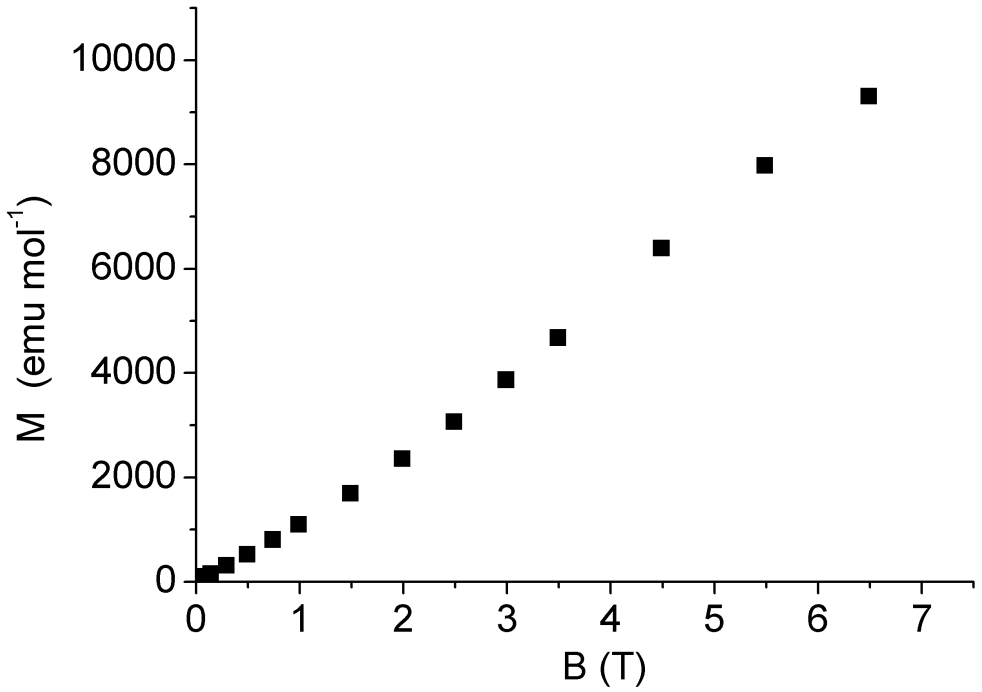

Figure S5. Field dependent magnetization curve for **1**, measured at 2 K. The inflection point around 4 T indicates the occurrence of the field induced spin state transition, from singlet to triplet.

ESI references

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