Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

SUPPORTING INFORMATION

Ferromagnetic Ni(II)-Cr(III) Single-chain magnet based on pentagonal bipyramid building units

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CONTENT :

Table S1 Crystallographic data for **1**-**4** and **[NiL^{N3O2Ph}]$_2$**

	[NiL^{N3O2Ph}]$_2$	**1**	**2**	**3**	**4**
Formula	$C_{46}H_{38}N_{10}Ni_2O_4$	$C_{23}H_{25}B_2F_8N_7Ni_1O_2$	$C_{27}H_{22}N_{11}Ni_2O_{0.50}$	$C_{73}H_{63}Cr_2N_{21}Ni_1O_6$	$C_{51}H_{47}Cl_1Cr_1N_{15}Ni_1O_7$
Mr	912.24	663.81	625.97	1493.14	1128.19
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Crystal color	red	orange	yellow	orange	orange
Space group	C 2/c	P 21/c	P 2_1/n	P 2_1/n	C 2/c
a/Å	22.4352(6)	14.874(1)	10.2821(5)	11.5125(3)	28.021(2)
b/Å	16.1038(2)	11.9090(9)	17.4266(7)	16.4374(3)	20.6609(10) Å
c/Å	15.4417(4)	15.814(1)	14.9144(6)	19.5359(4)	20.235(1)
α /°	90	90	90	90	90
β /°	133.251(5)	109.989(3)	102.068(2)	106.980(2)	96.273(2)
γ/°	90	90	90	90	90
V/Å^3	4063.5(4)	2632.4(4)	2613.3(2)	3535.7 (1)	11644(1)
Z	4	4	4	2	8
T/K	180	107	100	100	100
ρ_{calcd}/gcm^{-1}	1.49	1.67	1.59	1.40	1.29
μ(Mo-Kα)mm^{-1}	1.637	0.832	1.484	0.634	0.616
Reflections measured	18728	55103	55318	104637	148165
Independent reflect. (Rint)	3025 (0.030)	6533 (0.052)	6471 (0.059)	11367 (0.115)	13403 (0.074)
Refl. with I > n σ(I)	2813, n=1.5	5008, n=3	4536, n=3	8067, n=3	9260, n=3
Nb restraints	0	0	154	0	0
Nb parameters	280	388	321	418	676
R_1/wR_2 (I > n σ(I))	0.028/0.027	0.049/0.050	0.072/0.076	0.101/0.111	0.069/0.073
Residual e- density (ē.Å^{-3})	0.29/-0.28	1,53/-1,37	2,15/-0,93	2.09/-1.52	1.44/-1.27
CCDC N°	1957997	1958001	1958000	1957999	1957998

Table S2 Results from the polyhedral shape analysis by SHAPE[2] for the heptacoordinated metal centers in **1**-**4**.

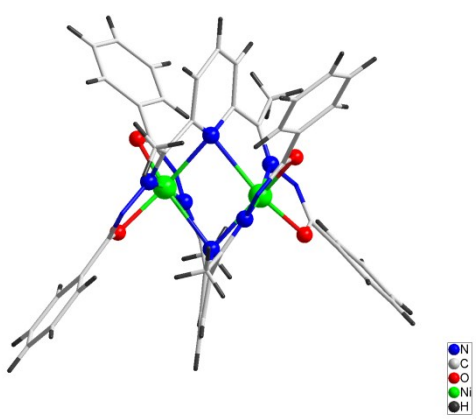
Complexes	PBPY-7[3]
$[NiL^{N5PhenMe}(H_2O)_2][BF_4]_2$ (**1**)	0.383
$[\{NiL^{N5PhenMe}\}\{Ni(CN)_4\}]_n$ $0.5H_2O$ (**2**)	0.302
$[\{NiL^{N5PhenMe}\}\{CrL^{N3O2Ph}(CN)_2\}_2].2H_2O$ (**3**)	Ni: 0.445 Cr: 0.371
$[\{NiL^{N5PhenMe}\}\{CrL^{N3O2Ph}(CN)_2\}].dmf.ClO_4$ (**4**)	Ni: 0.469 Cr: 0.298

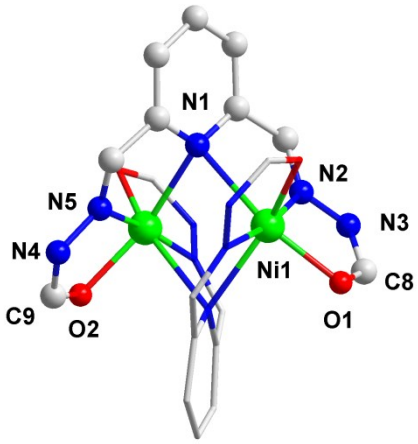
PBPY stands for pentagonal bipyramid

[2] SHAPE: Program for the stereochemical analysis of molecular fragments by means of continuous shape measures and associated tools; M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, 2.1 ed., University of Barcelona, Barcelona, **2013**.

[3] D. Casanova, P. Alemany, J. M. Bofill, S. Alvarez, *Chem. Eur. J.* **2003**, *9*, 1281-1295.

Figure S1 $[NiL^{N3O2Ph}]_2$: Molecular structure.

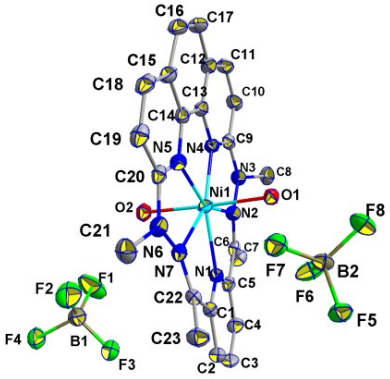


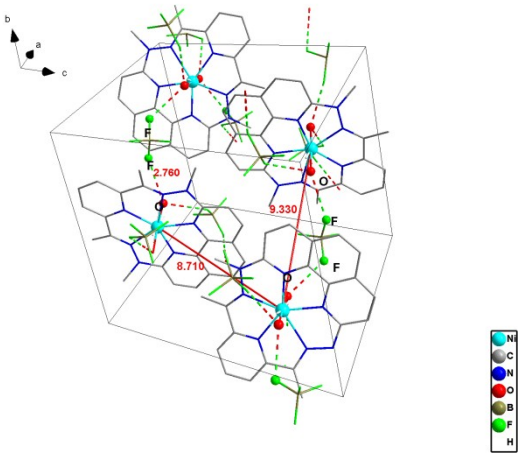


Selected bond distances (Å) and angles (°).

Ni1	N2	1.956(1)	N3	C8	1.330(2)
	$N5^{1-x, y, 1.5-z}$	1.964(1)	N4	C9	1.338(3)
	$O2^{1-x, y, 1.5-z}$,	2.019(2)	O2	C9	1.274(2)
	O1	2.0263(9)	O1	C8	1.283(2)
	$N1^{1-x, y, 1.5-z}$	2.291(2)	Ni-N1-$Ni^{1-x,y,1.5-z}$		81.26(4)
	N1	2.414(1)			
N2	N3	1.381(2)	N3-C8-O1, 126.1(1)		
N4	N5	1.383 (2)	N4-C9-O2, 125.8(1)		

Figure S2 [NiL^{N5PhenMe}(H_2O)$_2$]·2BF_4, **1**: ORTEP view of the asymmetric unit (ellipsoids are drawn at 50 % probability level) and crystal packing.

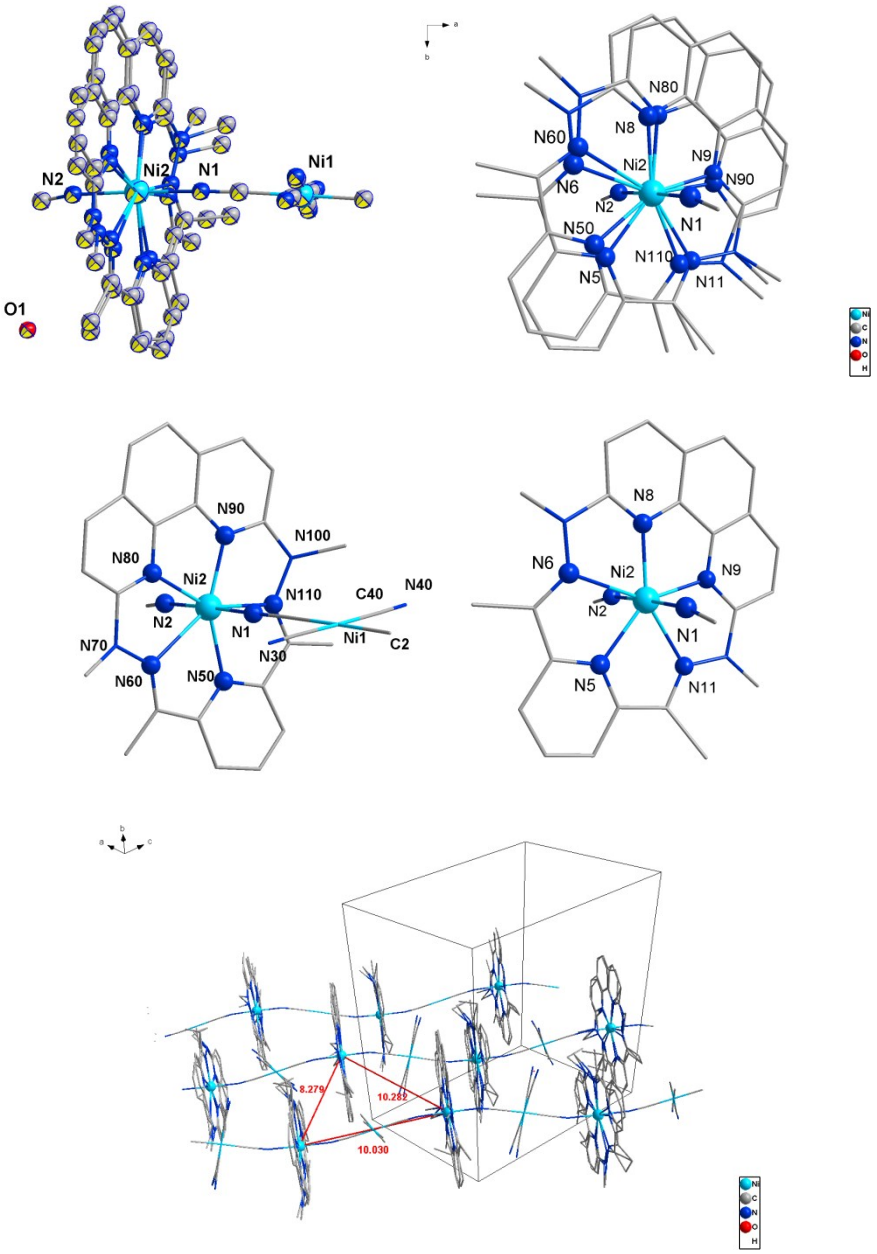




Selected bond distances (Å)

Ni1	N4	2.030(2)	N4	C13	1.361(3)
	O2	2.080(2)		N3	2.306(3)
	O1	2.098(2)		C14	2.362(3)
	N5	2.123(2)		C10	2.384(3)
	N1	2.132(2)		C12	2.415(3)
	N2	2.213(2)		N2	2.508(3)
	N7	2.434(2)		N5	2.627(3)
N1	C1	1.336(3)		C11	2.750(3)
	C5	1.352(3)	N5	C20	1.320(3)
	C2	2.381(3)		C14	1.358(3)
	C4	2.390(3)		N6	2.302(3)
	C22	2.403(3)	N5	C13	2.363(3)
	C6	2.427(3)		C19	2.392(3)
	N7	2.591(3)		C15	2.424(4)
	N2	2.6055(30)		N7	2.522(3)
	C3	2.755(3)		N4	2.627(3)
N2	C6	1.279(3)		C18	2.763(3)
	N3	1.385(3)	N6	N7	1.362(3)
	C9	2.299(3)		C20	1.385(3)
	C5	2.305(3)		C21	1.474(3)
	C8	2.493(3)		N5	2.302(1)
N2	N4	2.508(3)		C22	2.355(2)
	C7	2.516(3)		C19	2.461(3)
	N1	2.605(3)	N7	C22	1.274(3)
N3	N2	1.385(3)		N6	1.362(3)
	C9	1.392(3)		C20	2.297(3)
	C8	1.472(3)		C1	2.301(3)
	N4	2.306(3)		C21	2.508(3)
	C6	2.358431		C23	2.513(3)
	C10	2.469(3)		N5	2.522(3)
N4	C9	1.312(3)		N1	2.591(3)

Figure S3 [{NiL^{N5PhenMe}}{Ni(CN)$_4$}]0.5H$_2$O, **2**: ORTEP view of the asymmetric unit (ellipsoids are drawn at 50 % probability level) and crystal packing.

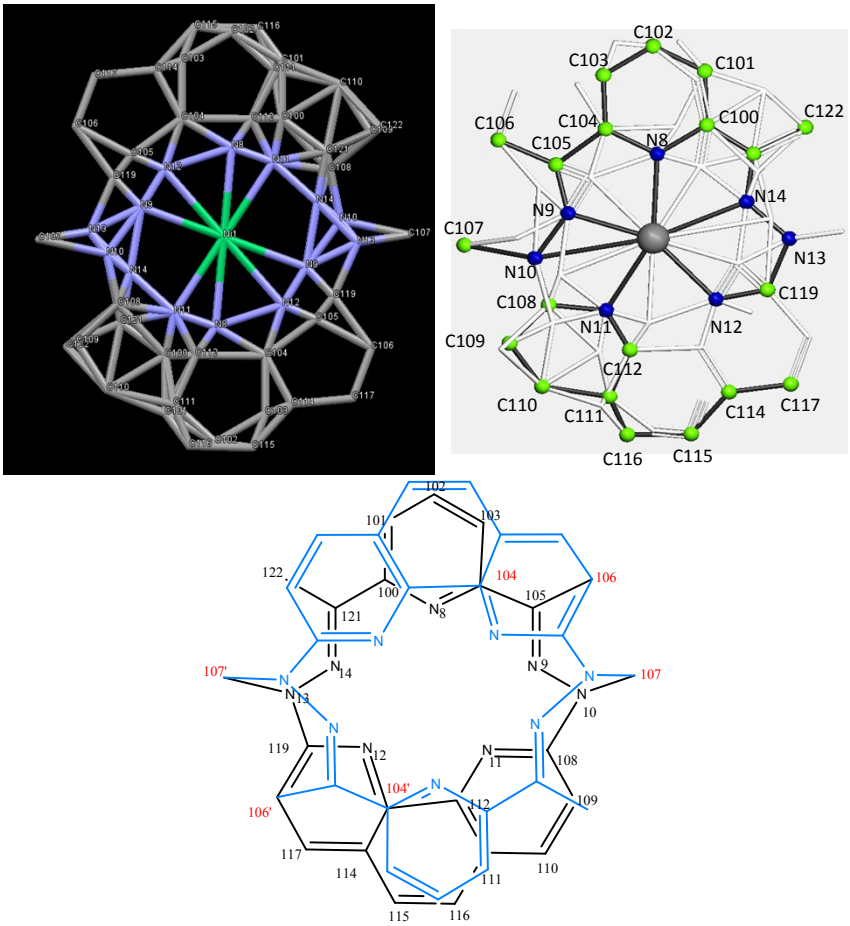


Selected bond distances (Å) and angles (°)

Ni2	N90	2.0387(64)	Ni2	N11	2.2621(59)
	N1	2.0462(48)		N6	2.3932(60)
	N9	2.0614(63)		N60	2.4846(58)
	N2	2.0638(48)	Ni2	Ni2$^{-0.5+x, 0.5-y, -0.5+z}$	8.2785(9)
	N8	2.0986(53)		Ni2$^{0.5+x, 0.5-y, 0.5+z}$	8.2785(9)
	N50	2.1475(91)		Ni2$^{0.5+x, 0.5-y, -0.5+z}$	10.0297(11)
	N80	2.1614(36)	N1-Ni2-N2, 177.7(2)		
	N110	2.1624(56)	Ni1-N1-Ni2, 166.1(2)		
	N5	2.1703(100)	Ni1-N2$^{0.5+x,0.5-y,-0.5+z}$-Ni2$^{0.5+x,0.5-y,-0.5+z}$, 166.0(2)		

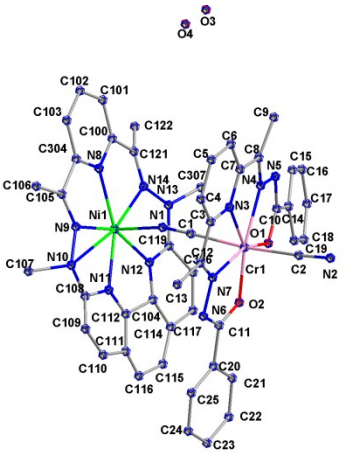
Figure S4 [{NiL^{N5PhenMe}}{CrL^{N3O2Ph}(CN)$_2$}$_2$].2H$_2$O, **3**. (**a**) detail of the disordered L^{N5PhenMe} ligand and best modeling, (**b**) ORTEP plots of asymmetric unit, (**c**) crystal packing.

(**a**)

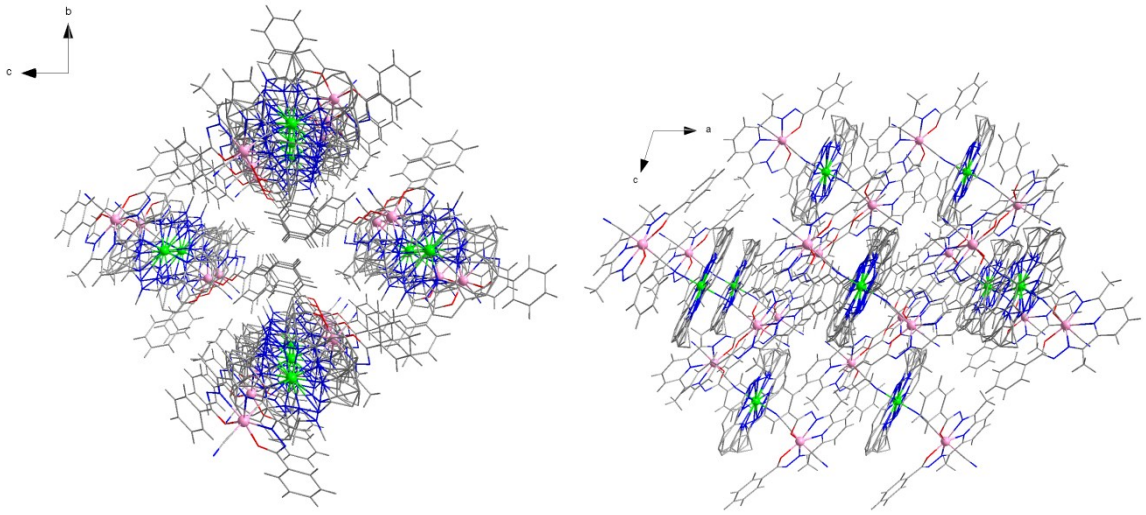


Atoms C104, C106, and C107 (in red in the sketch) have occupancy of 1 while all the other positions have occupancy of 0.5. Symmetry code: ' = 1-x, 2-y, 1-z

(**b**)



(**c**)



Shortest intermolecular distances between metal enters:

Cr1-Cr1$^{2-x,2-y,1-z}$, 8.284(1) Å; Cr1-Ni1$^{1+x,y,z}$, 8.5635(7) Å

Selected bond distances (Å) and angles (°)

Ni1	N1	2.0753(42)
	N8	2.1661(62)
	N9	2.1194(114)
	N11	2.1673(86)
	N12	2.1661(84)
	N14	2.406(8)

Ni1-N1-C1, 165.50(38)

Cr1	N3	2.3954(36)
	N4	2.1993(38)
	N7	2.2296(32)
	O1	1.9430(31)
	O2	1.962(3)
	C1	2.0628(31)
	C2	2.0827(42)

Cr1-N1-C1, 172.89(35)

Cr1-N2-C2, 175.24(41)

C1-Cr1-C2, 174.39(16)

Figure S5 Powder X-Ray patterns for [{NiL^{N5PhenMe}}{CrL^{N3O2Ph}(CN)$_2$}$_2$].2H$_2$O, **3** : (up) experimental diffractogram (blue line) obtained from the crystals batch and (down) calculated diffractogram (red line) deduced from the single crystal X-Ray diffraction.

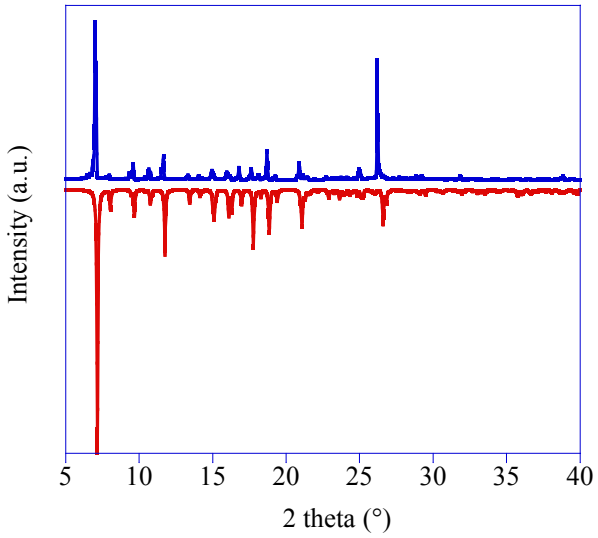
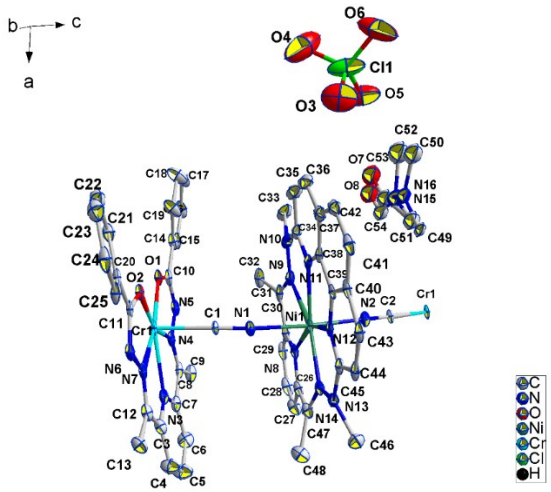
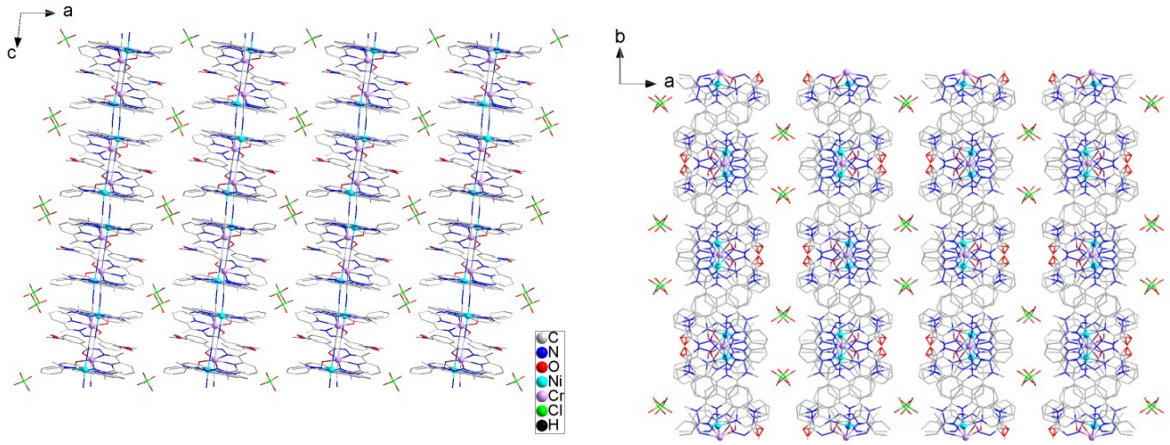


Figure S6 [{NiL^{N5PhenMe}}{CrL^{N3O2Ph}(CN)$_2$}].dmf.ClO$_4$, **4**: (**a**) ORTEP plot of asymmetric unit (ellipsoids are drawn at the 30% probability level), (**b**) Crystal packing, (**c**) inter-chain arrangement and relative organization of the Ni moieties, the colored surfaces materialize the plane crossing the atoms N8, N11 and N12 of the [NiL^{N5PhenMe}] moieties.

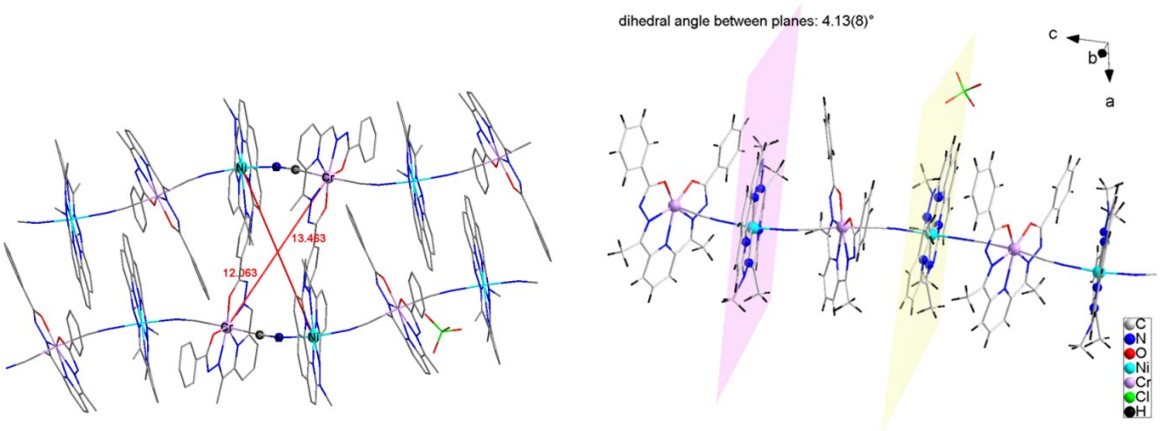
(**a**)



(**b**)



(**c**)



Selected bond distances (Å) and angles (°)

Ni1	N1	2.0639(29)	Cr1	N3	2.3900(33)
	N2	2.0704(29)		N4	2.2313(29)
	N8	2.1365(32)		N7	2.2077(32)
	N9	2.5553(34)		O1	1.9524(28)
	N11	2.2053(33)		O2	1.9594(24)
	N12	2.0094(27)		C1	2.0554(30)
	N14	2.1054(34)		C2	2.0641(31)

N1-Ni1-N2, 170.16(11)
Ni1-N1-C1, 170.71(26)
Ni1-N2-C2, 167.47(27)

Cr1-N1-C1, 172.31(27)
Cr1-N2-C2, 171.65(27)
C1-Cr1-C2, 163.86(12)

Figure S7 Powder X-Ray patterns for [{NiL^{N5PhenMe}}{CrL^{N3O2Ph}(CN)$_2$}].dmf.ClO$_4$, **4** : (up) experimental diffractogram (blue line) obtained from the crystals batch and (down) calculated diffractogram (red line) deduced from the single crystal X-Ray diffraction.

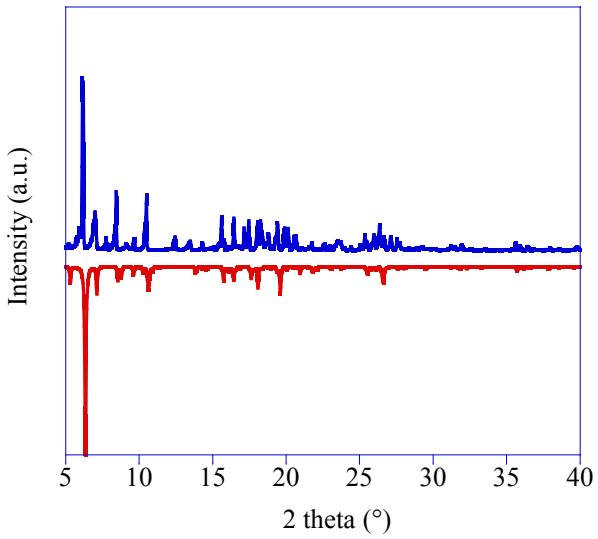
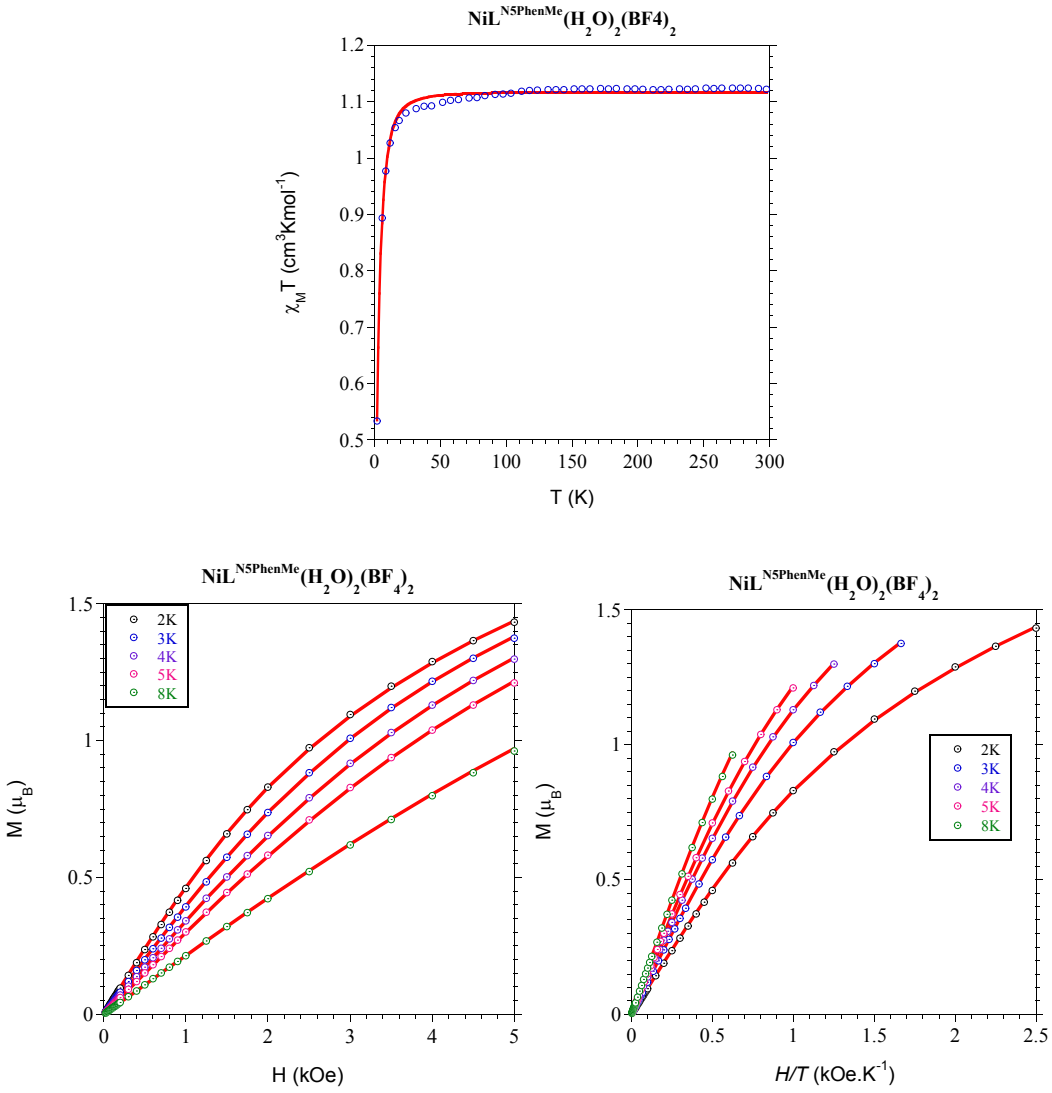


Figure S8 Magnetic behavior for $[NiL^{N5PhenMe}(H_2O)_2]\cdot 2BF_4$, **1**. Experimental (O) and calculated (–) temperature dependence of $\chi_M T$, and isothermal magnetizations.

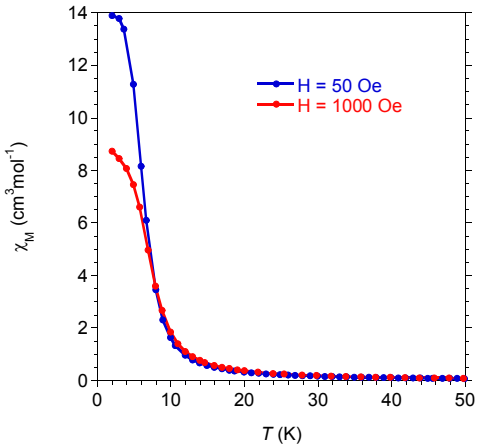
Best fit[4] parameters: D = -10.95 ± 0.04 cm^{-1}, E = 1.515 ± 0.008 cm^{-1}, g = 2.11.



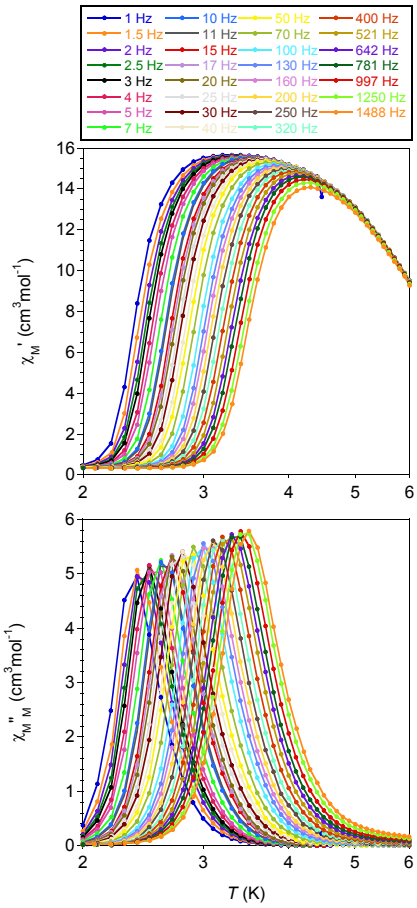
[4] Performed with PHI: N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, PHI: A powerful new program for the analysis of anisotropic monomeric and exchange-coupled polynuclear d- and f-block complexes, *J. Comput. Chem.*, 2013, **34**, 1164-1175.

Figure S9 Additional magnetic data for [{NiL^{N5PhenMe}}{CrL^{N3O2Ph}(CN)$_2$}].dmf.ClO$_4$, **4**.

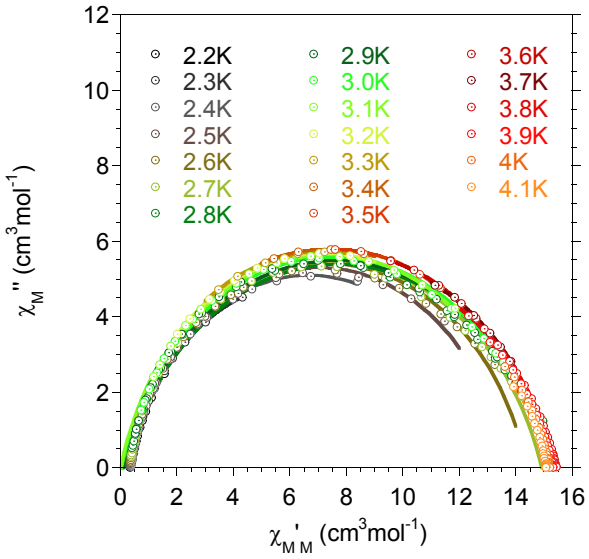
1. Temperature dependence of the molar magnetic susceptibility (χ_M) with H_{dc} = 1 kOe (red) and H_{dc} = 50 Oe (blue).



2. Temperature dependence of χ_M' and χ_M'' for AC frequencies between 1 and 1500 Hz with H_{ac} = 3 Oe.



3. Cole-Cole plots and best-fit parameters



T (K)	χ_T	χ_S	α
2.2	14.607	0.343	0.161
2.3	12.494	0.341	0.137
2.4	12.990	0.334	0.136
2.5	13.174	0.317	0.147
2.6	14.391	0.280	0.167
2.7	14.920	0.206	0.192
2.8	15.291	0.089	0.215
2.9	15.033	0.081	0.191
3.0	14.985	0.019	0.183
3.1	14.670	0.010	0.164
3.2	14.333	0.048	0.145
3.3	14.264	0.058	0.136
3.4	14.621	0.017	0.147
3.5	14.892	0.114	0.153
3.6	15.044	0.570	0.151
3.7	15 .410	0.031	0.197
3.8	15.434	1.248	0.195
3.9	15.313	2.935	0.172
4.0	15.189	5.099	0.139
4.1	15.07	6.661	0.119
4.2	14.92	6.873	0.126