Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Enhancement of coordinating flexibility in a Schiff–Mannich combo ligand: Forced generation of new $Ni^{II}–O_{phenoxo}–Ln^{III}–O_{alkoxo}–Ln^{III}$ array (Ln = Gd, Tb, Dy and Ho)

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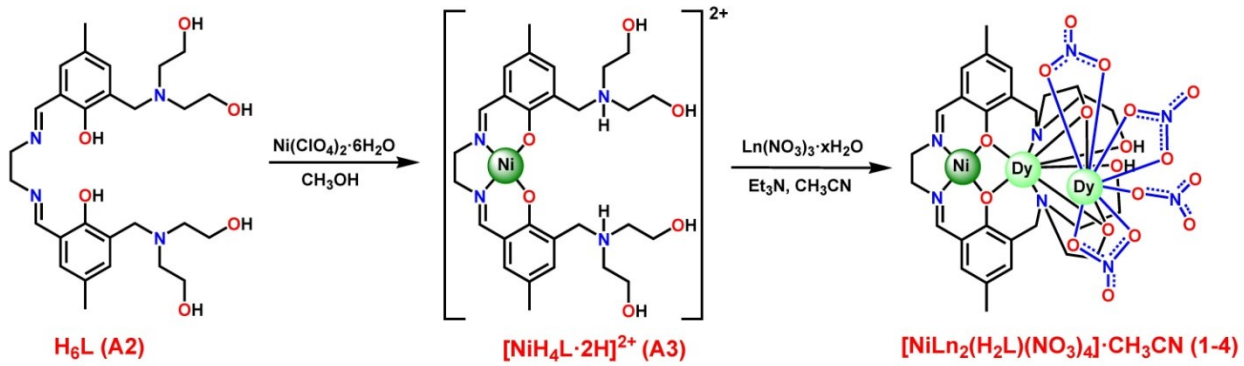


Scheme S1 Synthetic route to complexes **1**–**4**.

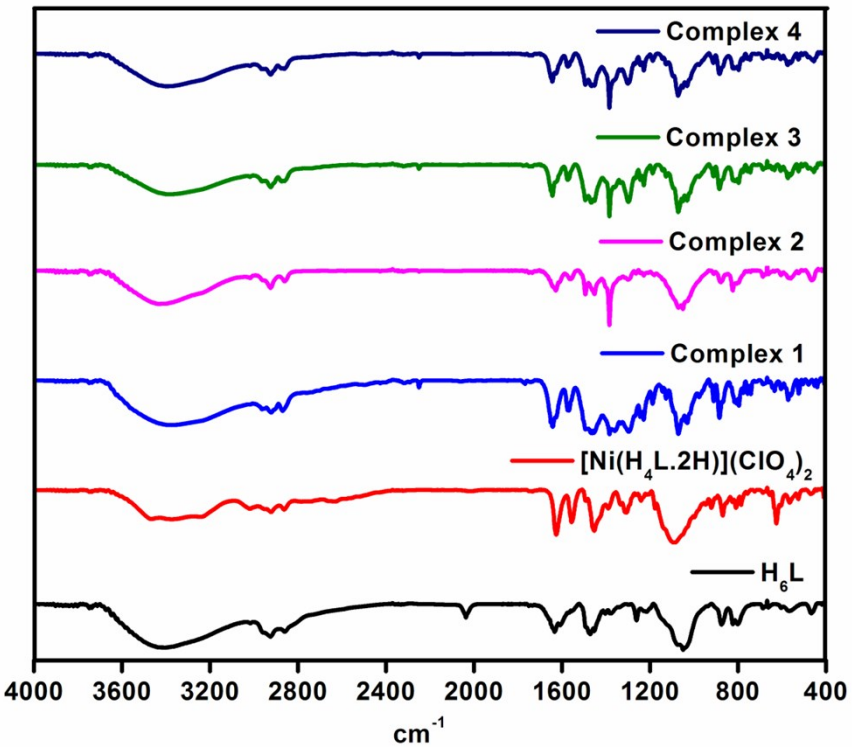


Fig. S1 FT−IR spectrum of H_6L, complexes $[Ni(H_4L{\cdot}2H)](ClO_4)_2$, **1**, **2**, **3** and **4**.

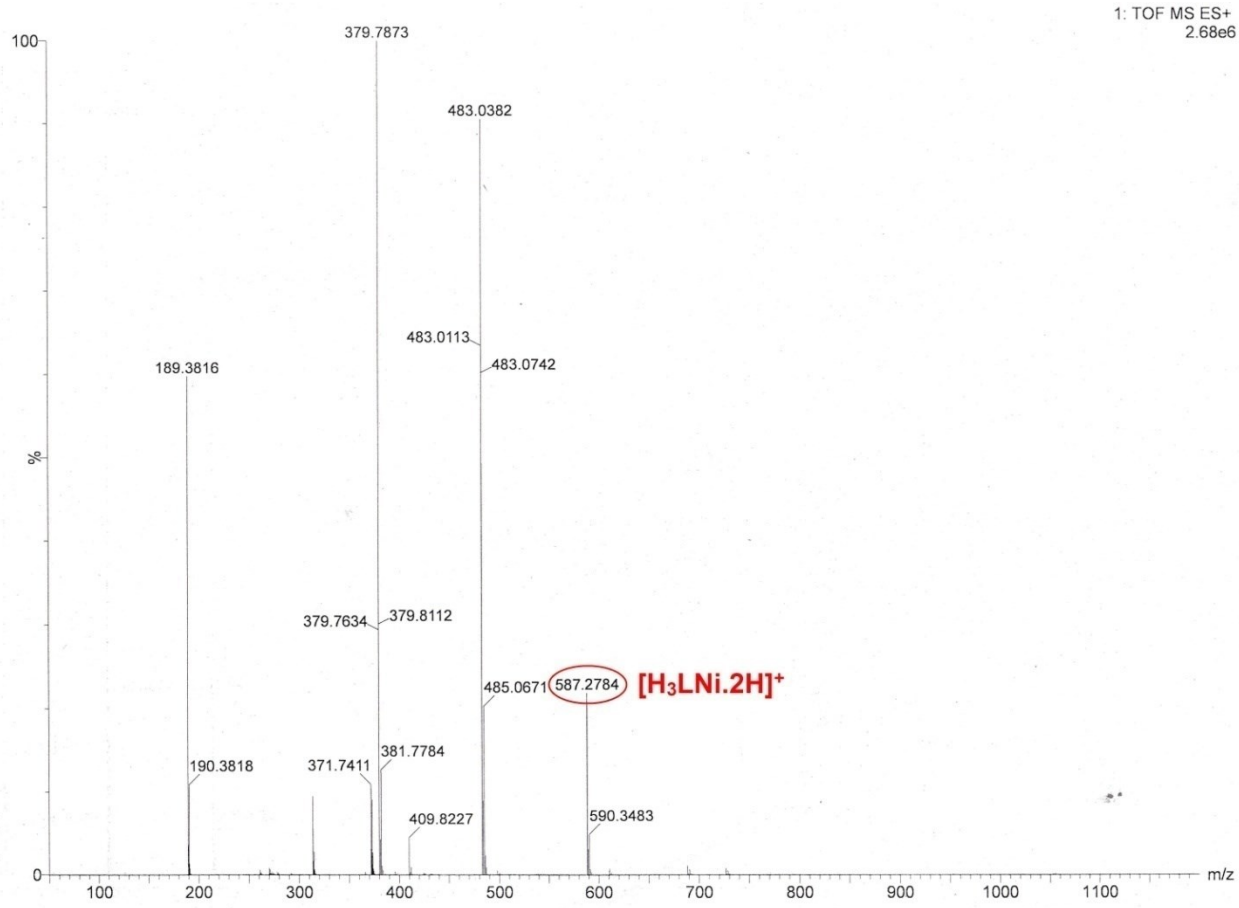


Fig. S2 ESI–MS spectrum of $[Ni(H_4L{\cdot}2H)](ClO_4)_2$ complex.

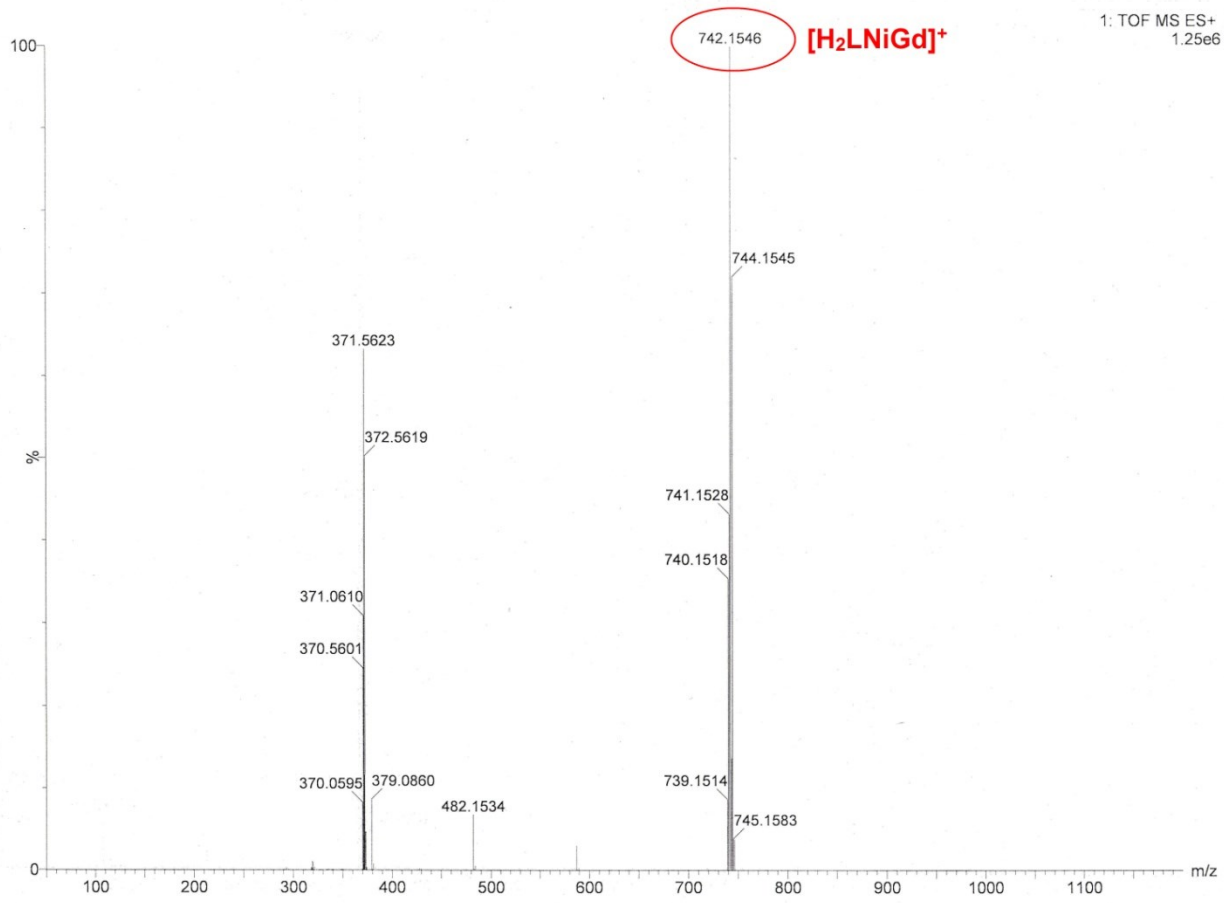


Fig. S3 ESI–MS spectrum of **1**.

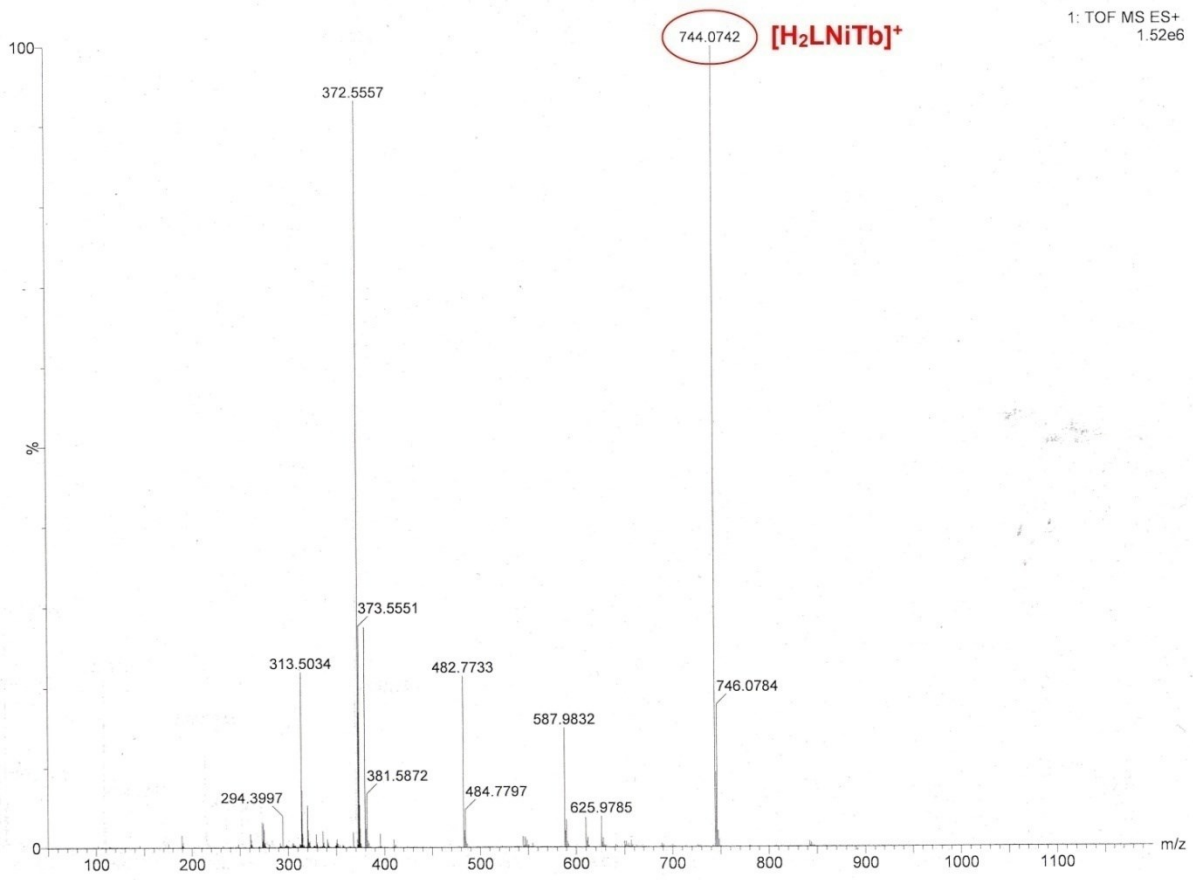


Fig. S4 ESI–MS spectrum of **2**.

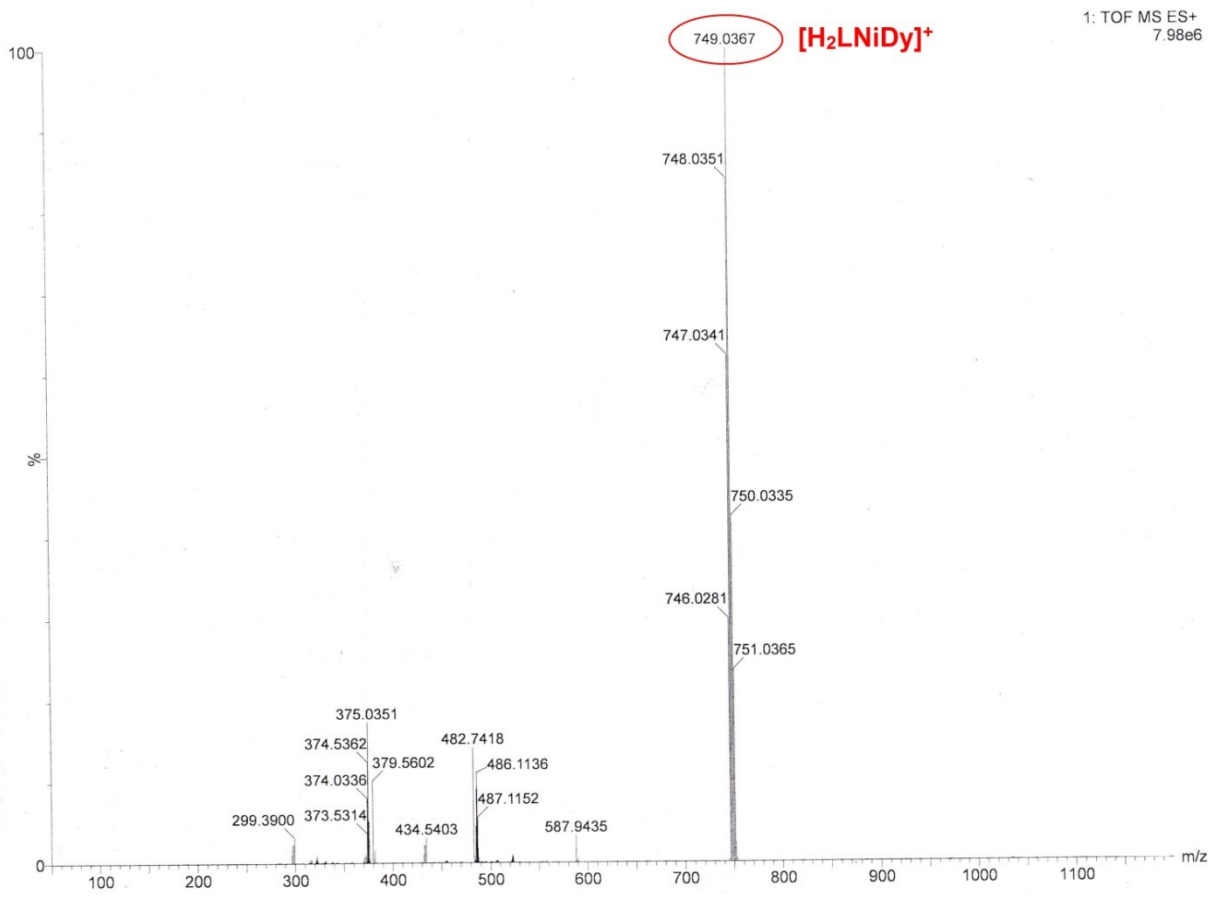


Fig. S5 ESI–MS spectrum of **3**.

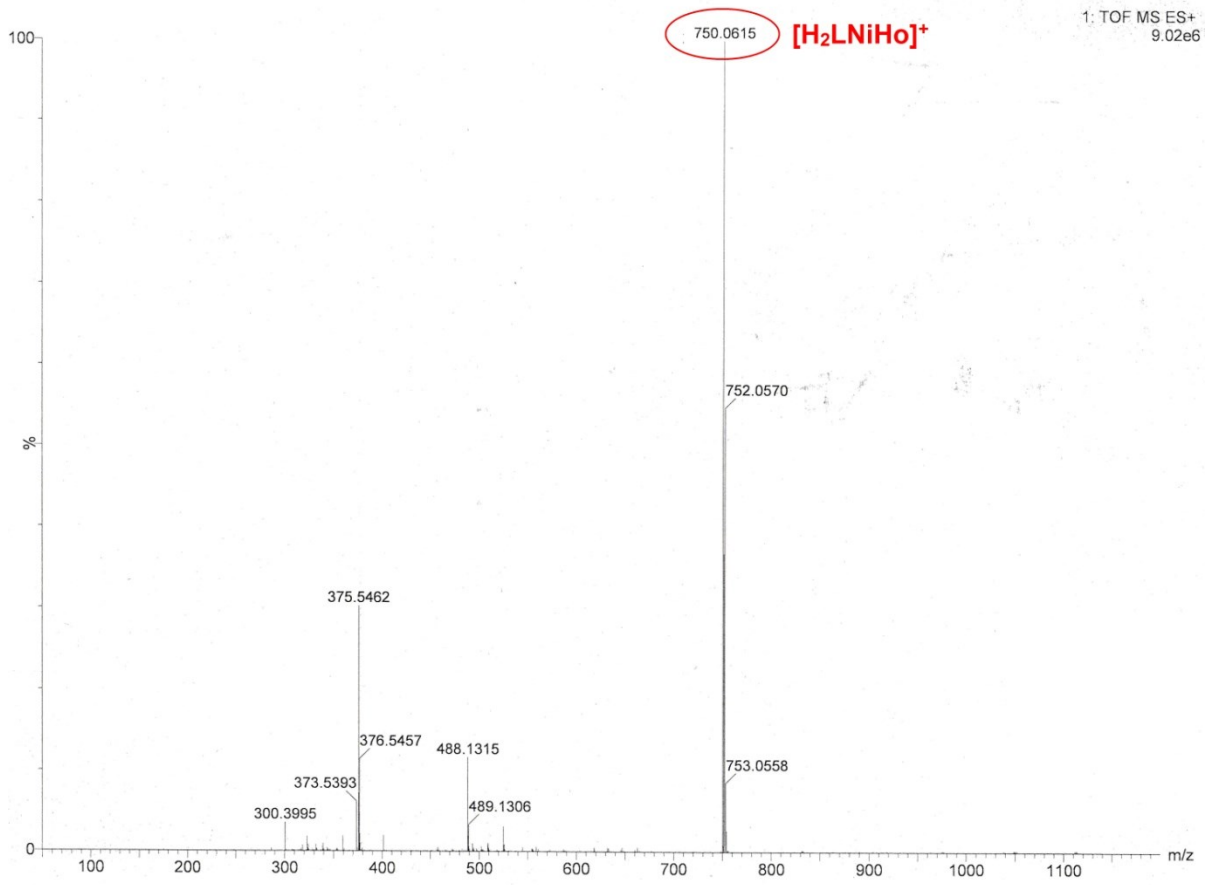


Fig. S6 ESI–MS spectrum of **4**.

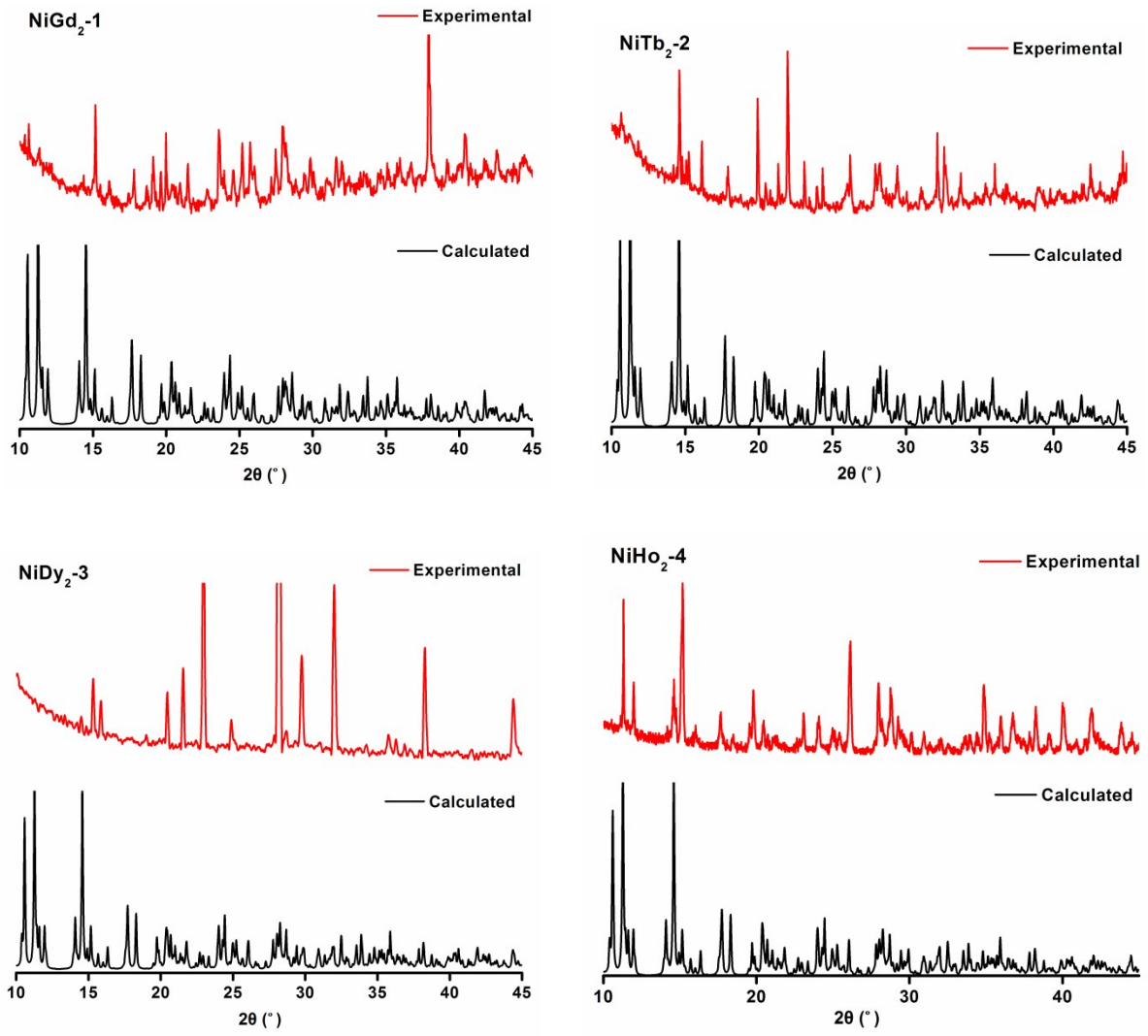


Fig. S7 Experimental (red) and calculated (black) Powder X–ray diffraction spectrum of complex **1**, **2**, **3** and **4** to determine the phase purity.

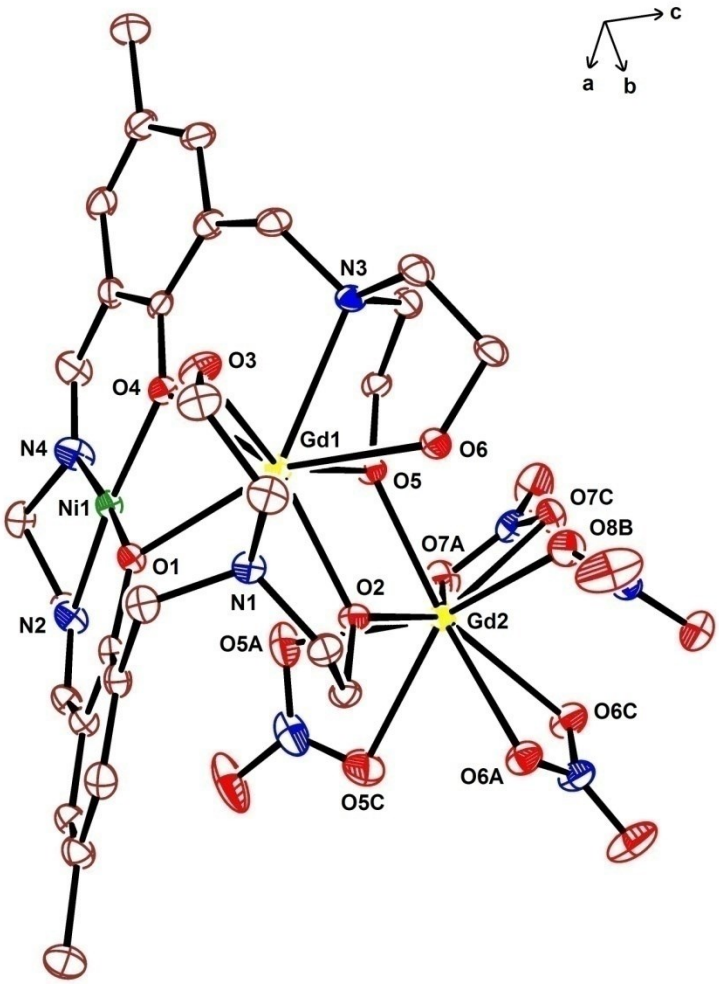


Fig. S8 Molecular structure of **1** with ellipsoids at the 20% probability level (Only the major component of the disorder is shown. Hydrogen atoms and solvent molecule were omitted for clarity).

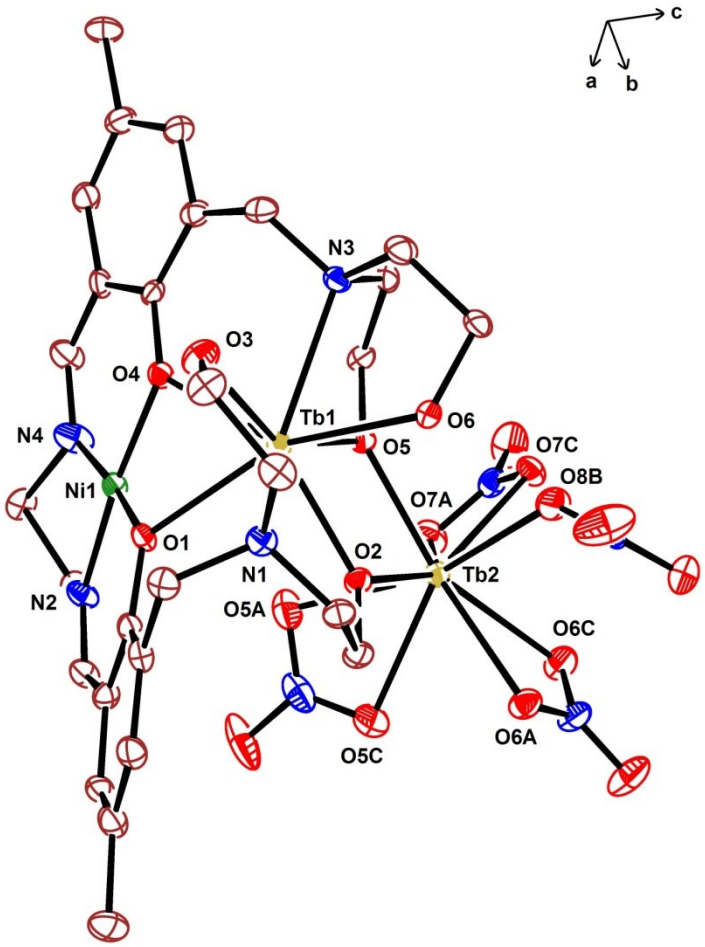


Fig. S9 Molecular structure of **2** with ellipsoids at the 20% probability level (Only the major component of the disorder is shown. Hydrogen atoms and solvent molecule were omitted for clarity)..

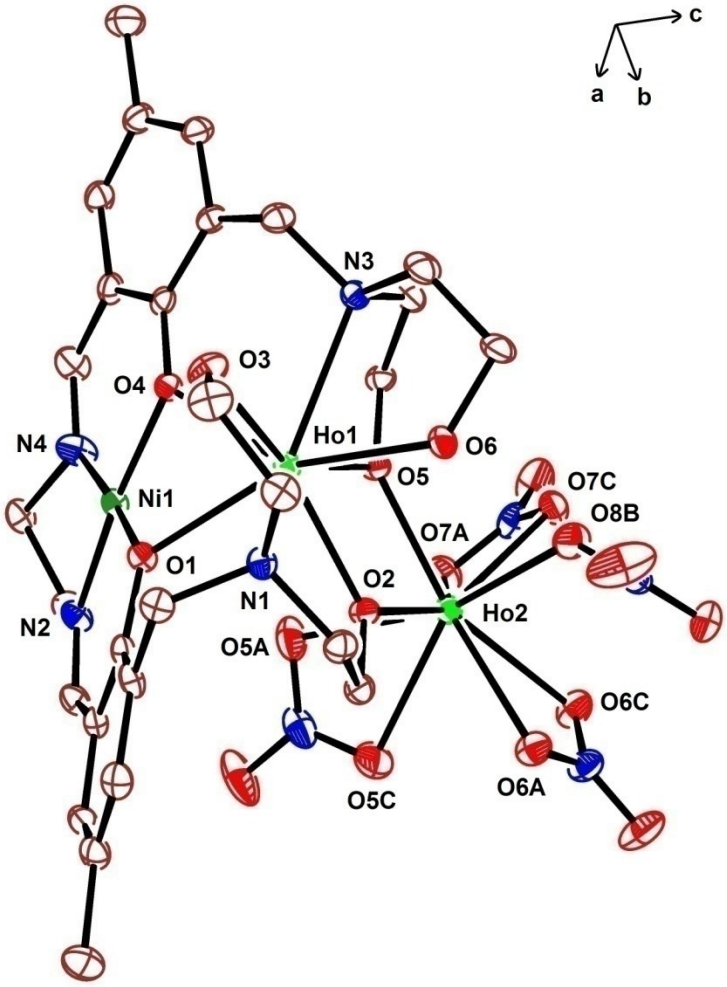


Fig. S10 Molecular structure of **4** with ellipsoids at the 20% probability level (Only the major component of the disorder is shown. Hydrogen atoms and solvent molecule were omitted for clarity).

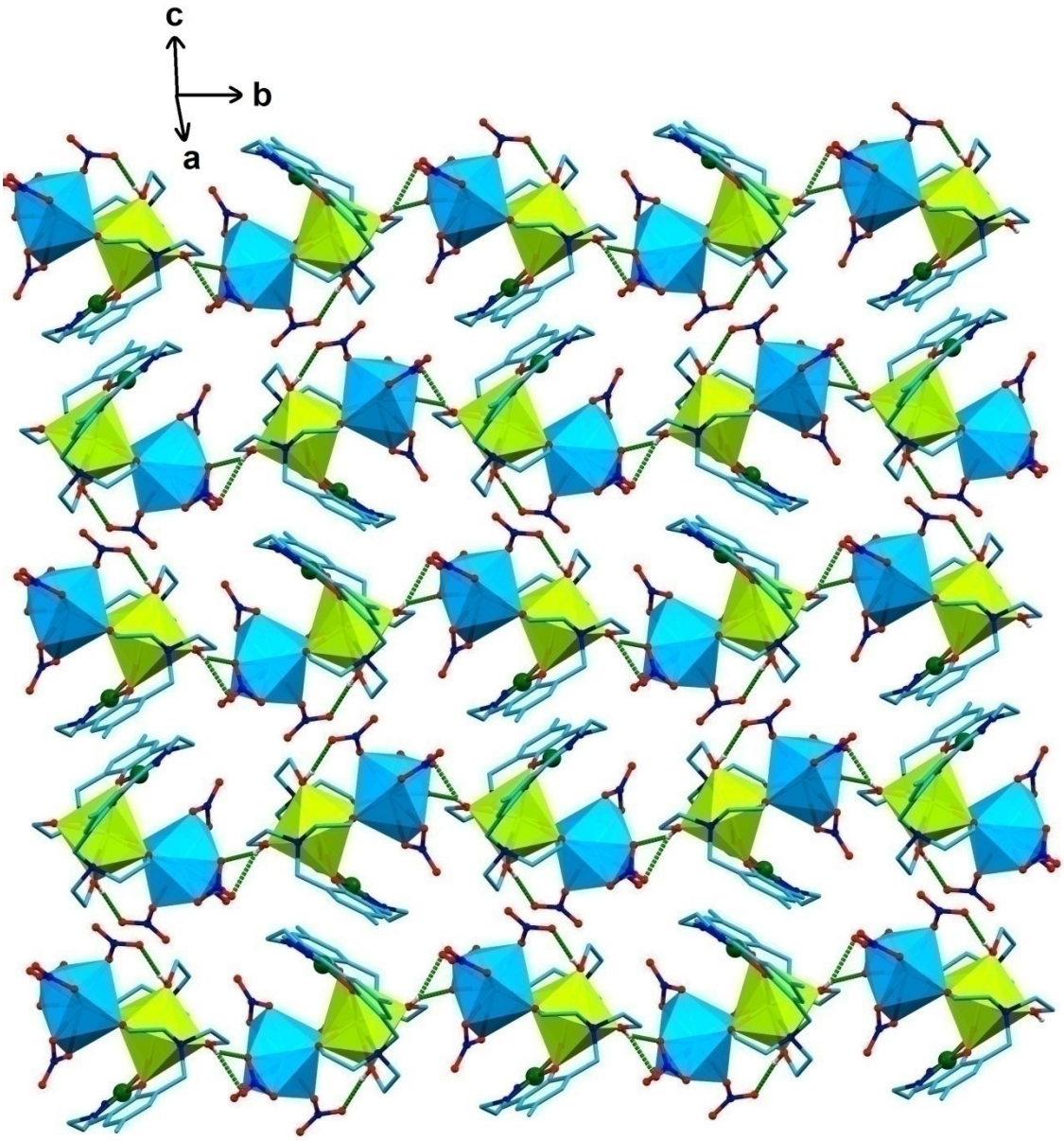


Fig. S11 A 2D corrugated sheet like structure formed by H–bonding and C–H···π interaction along crystallographic axis *b* and *c* respectively.

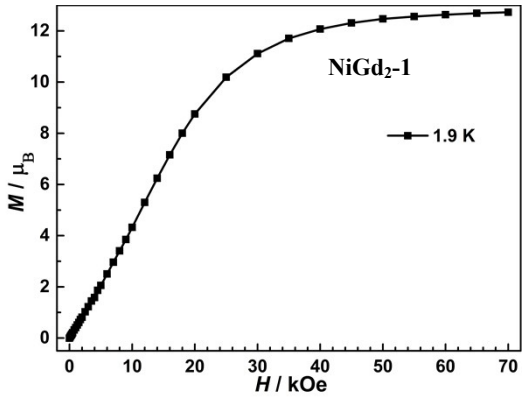


Fig. S12 Field dependence of magnetization for complex **1** at 1.9 K.

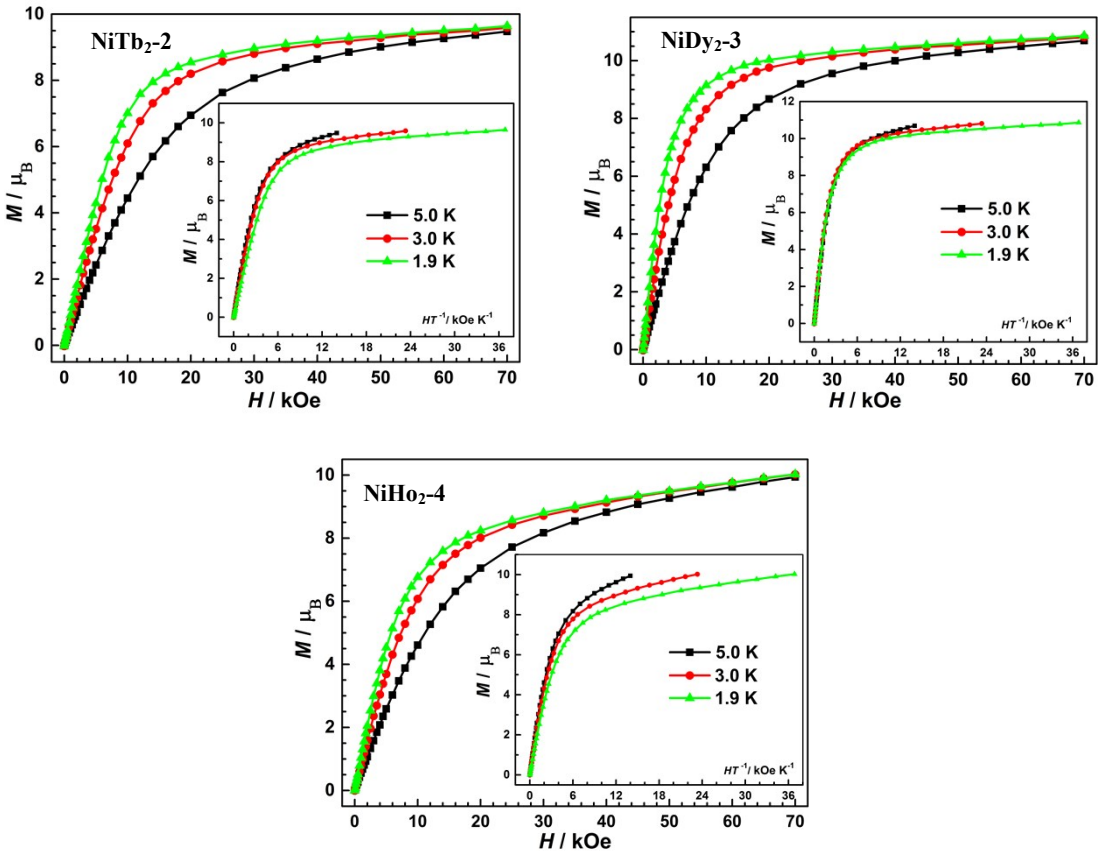


Fig. S13 Field dependence of magnetization for complexes **2**–**4** at 1.9, 3.0 and 5 K. Inset: plots of the reduced magnetization M versus HT^{-1}.

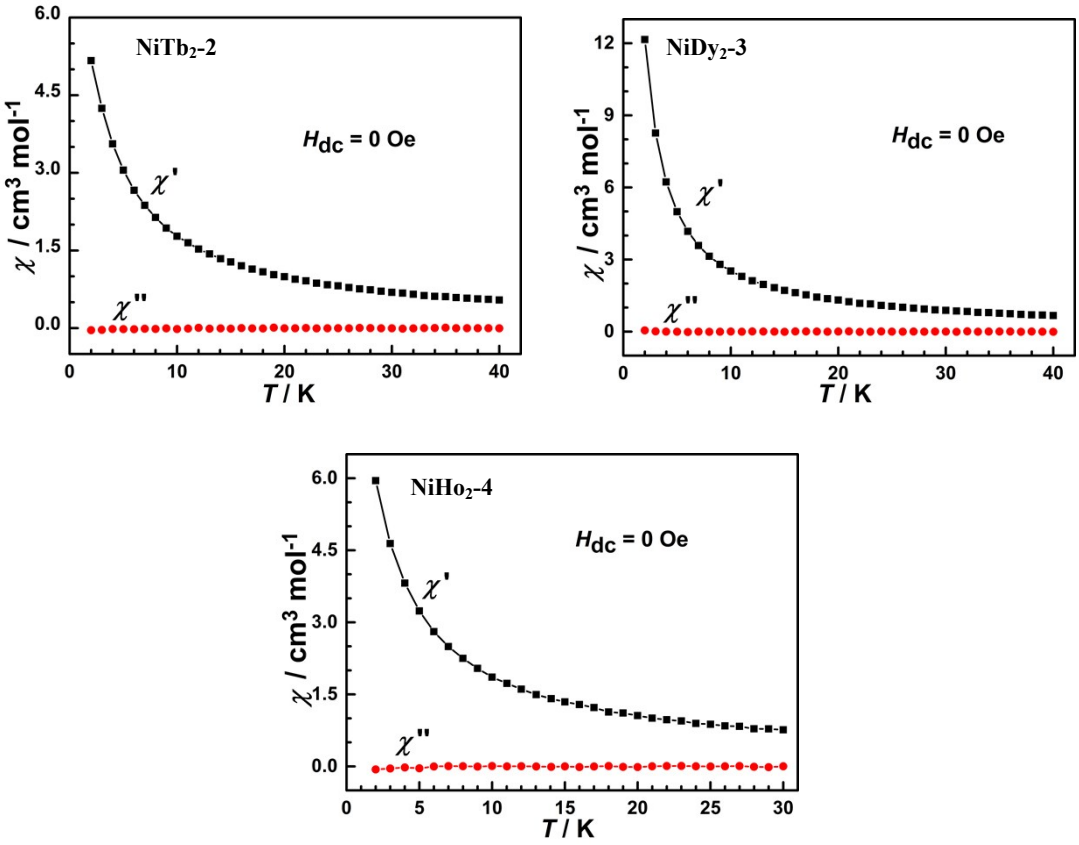


Fig. S14 Temperature dependence of in–phase (χ') and out–of–phase (χ'') ac signals for complexes **2**–**4** under a zero dc field at 997 Hz and 1.9 K.

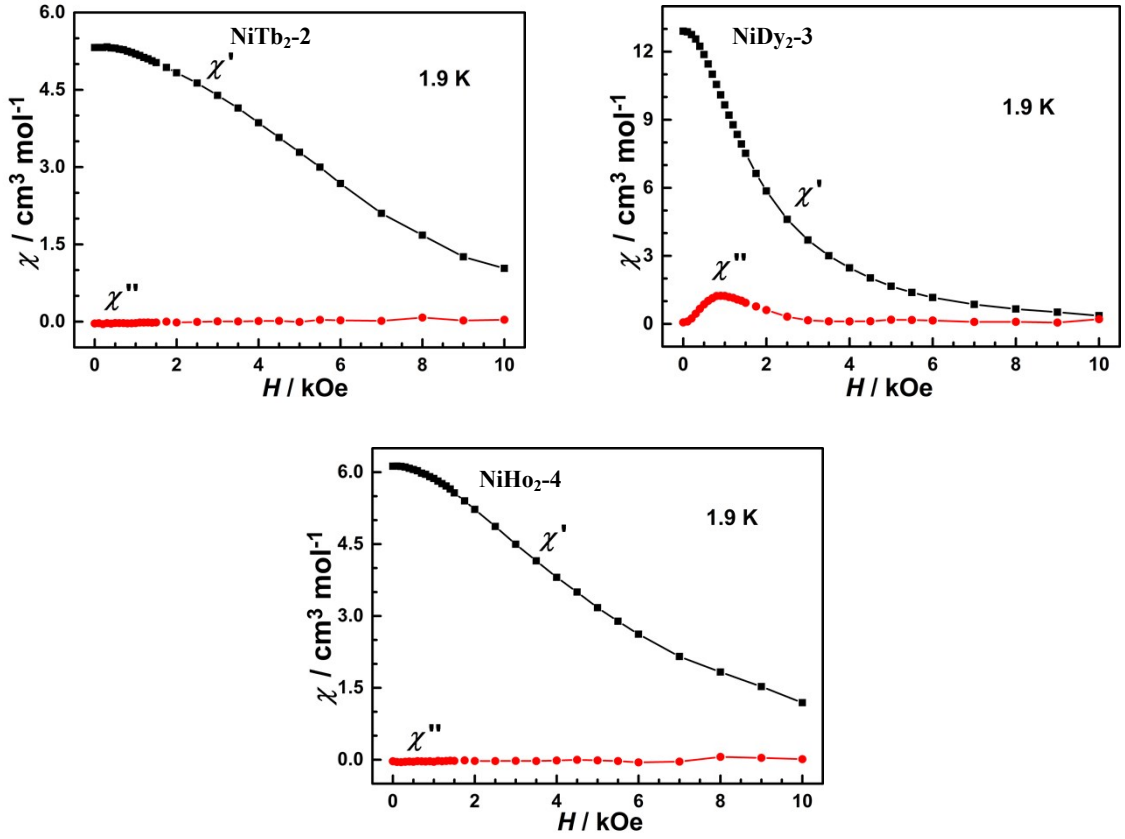


Fig. S15 Field dependence of in–phase (χ') and out–of–phase (χ'') ac signals for complexes **2**–**4** at 997 Hz and 1.9 K.

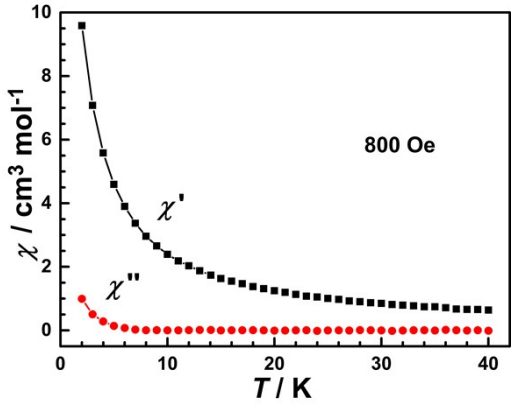


Fig. S16 Temperature dependence of χ' and χ'' ac signals for complex **3** under a 800 Oe dc field at 997 Hz.

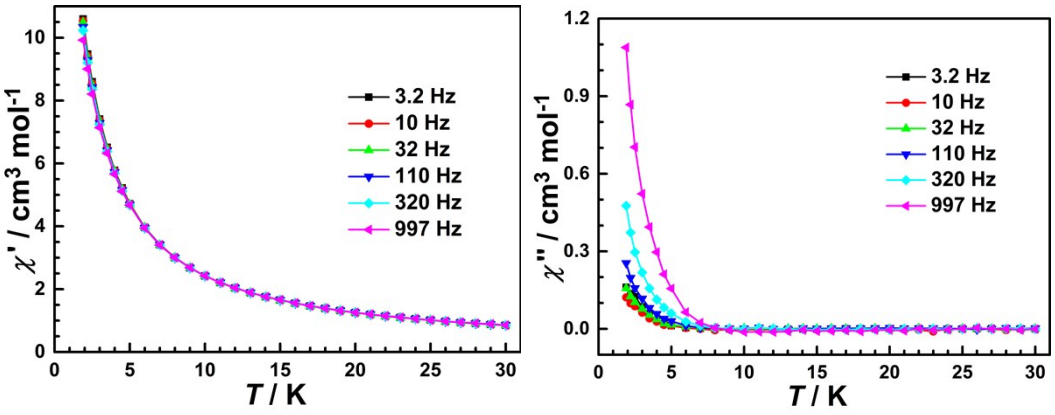


Fig. S17 Temperature dependence of χ' (left) and χ'' (right) ac signals for complex **3** under a 800 Oe dc field.

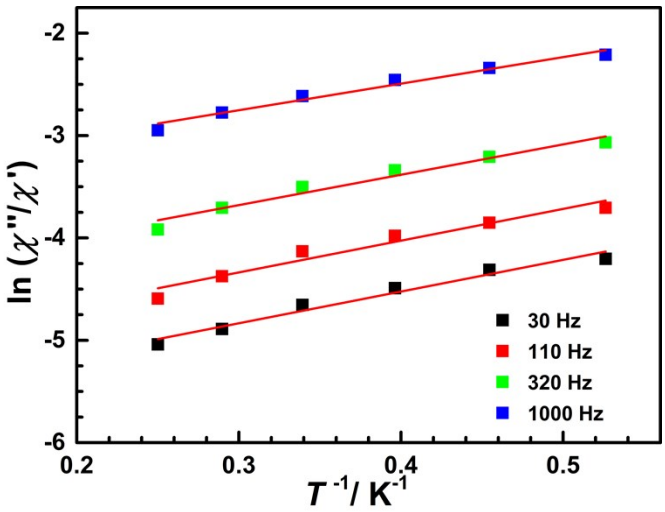
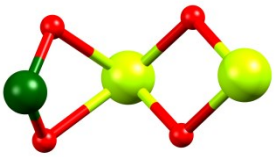
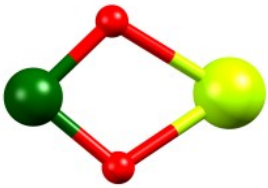
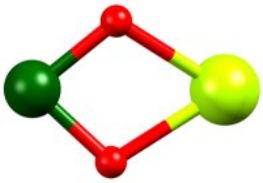
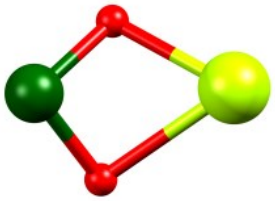
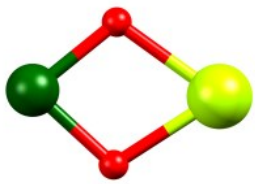
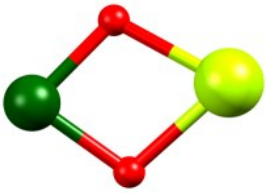
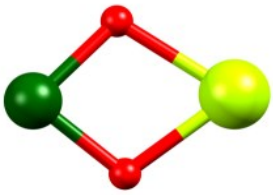
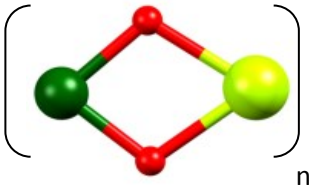
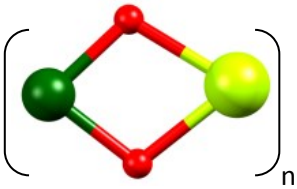
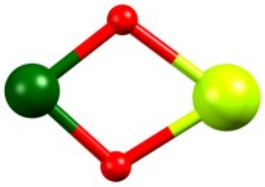
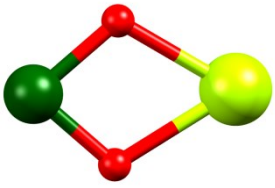
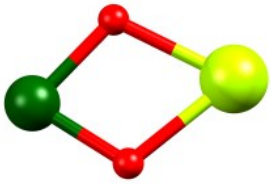
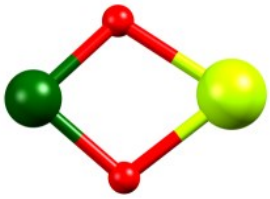
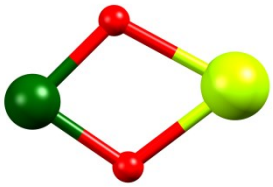
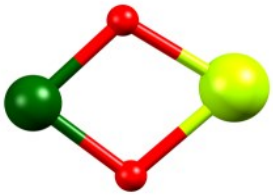
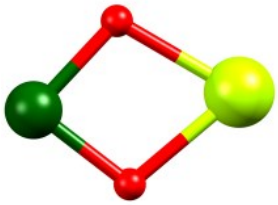
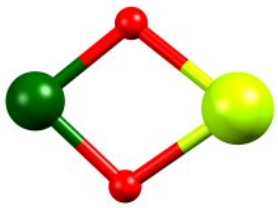


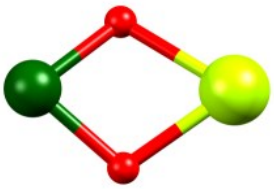
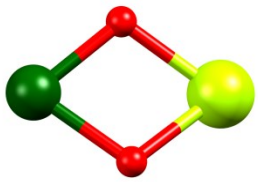
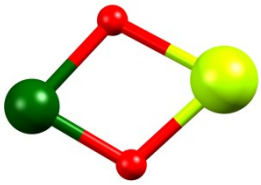
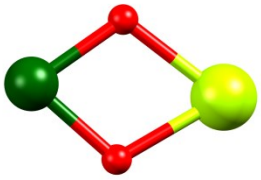
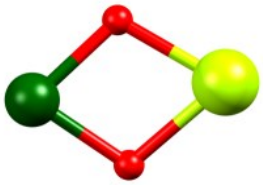
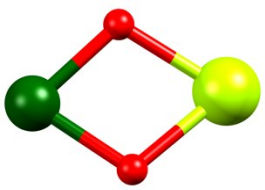
Fig. S18 Plots of ln (χ''/χ') vs. $1/T$ for complex **3** under a 800 Oe dc field. The solid line represents a fit of the results in the range of 30–1000 Hz.

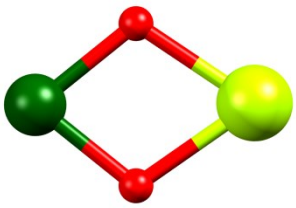
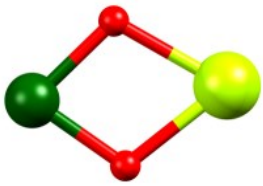
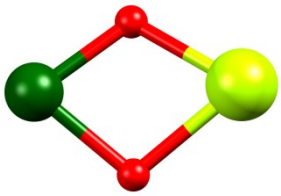
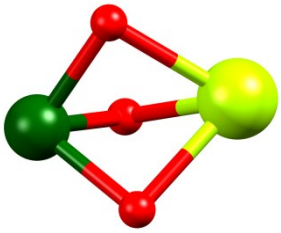
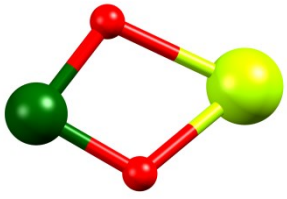
Table S1 $Ni_x^{II}Ln_y^{III}$ complexes found in literature with their magnetic property.

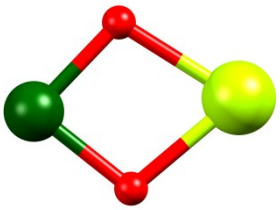
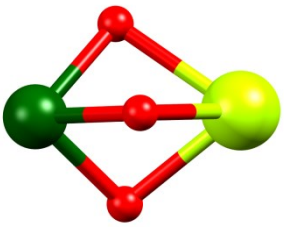
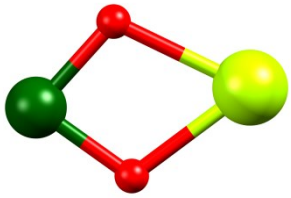
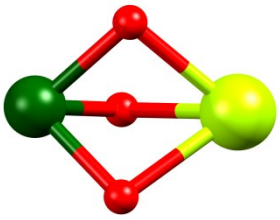
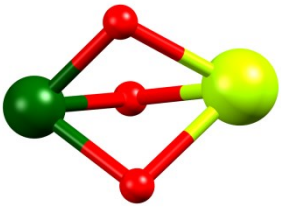
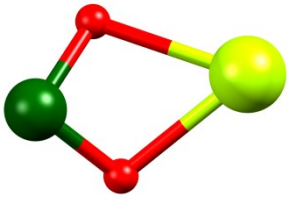
Sl. No.	Ni^{II}/Ln^{III}core	Ln^{III}	Magnetic property of $Ni_x^{II}Ln_y^{III}$ complexes	Reference
1		Gd, Tb, Dy, Ho	Slow magnetic relaxation [$NiDy_2$] U_{eff} [$NiDy_2$] = 2.94 K	This work
		NiLn		
1		Ce, Nd, Dy, Er, Yb, Eu	Slow magnetic relaxation [NiCe], [NiNd], [NiDy], [NiEr], [NiYb], U_{eff} [NiCe] = 4.7 K U_{eff} [NiNd] = 15.9 K U_{eff} [NiDy] =7.7 K	*Dalton Trans.*, 2019, **48**, 641
2		Ce, Gd, Dy	Slow magnetic relaxation [NiLn]	*Dalton Trans.*, 2019, **48**, 13943
3		Tb, Eu, Gd, Ho	Single molecule magnet [NiTb] U_{eff} [NiTb] = 7.69 K Ferromagnetic [NiGd] J_{NiGd} = + 0.87 cm^{-1}	*Dalton Trans.*, 2017, **46**, 12558
		Tb, Dy, Eu, Gd, Ho	Single molecule magnet [NiDy] U_{eff} [NiDy] = 5.14 K Ferromagnetic [NiGd] J_{NiGd} = + 1.83 cm^{-1}	

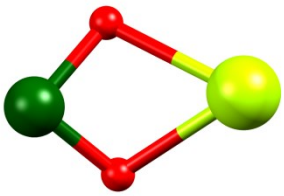
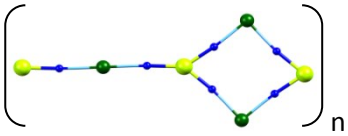
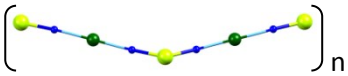
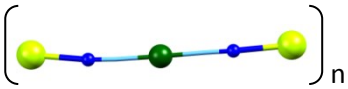
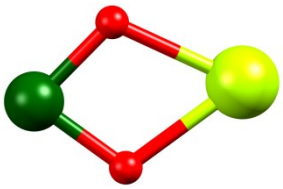
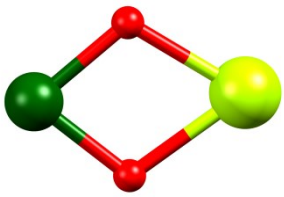
		La, Dy	Antiferromagnetic [NiDy]	
4		Dy	Antiferromagnetic	*New J. Chem.*, 2016, **40**, 6998
		La, Tb	Ferromagnetic $[NiTb]_n$	
5		Gd, Dy	Slow magnetic relaxation [NiDy]	*CrystEngComm*, 2016, **18**, 4779
6		Gd, Tb, Dy	Single molecule magnet [NiDy] U_{eff} = 16.9 K	*New J. Chem.*, 2015, **39**, 3467
7		Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb	Single molecule magnet [NiTb], [NiDy]	*Inorg. Chim.* Acta, 2015, **435**, 274

8		Gd	Ferromagnetic J_{NiGd} = + 1.31 cm^{-1}	*Chem. Eur. J.*, 2014, **20**, 14235
9		Tb, Gd, Dy, Ho, Er, Y	Slow magnetic relaxation [NiTb], [NiDy], [NiHo]	*Dalton Trans.*, 2014, **43**, 8921
10		Gd, Pr	Ferromagnetic [NiGd] Antiferromagnetic [NiPr]	*Dalton Trans.*, 2014, **43**, 17375
11	 	Eu, Gd, Dy, Ho, La, Sm, Eu	Ferromagnetic [NiGd] J_{NiGd} = 1.56 cm^{-1} –	*New J. Chem.*, 2013, **37**, 2280
12		Gd, Tb, Dy	Single molecule magnet [NiTb] U_{eff} = 14.9 K	*Inorg. Chem.*, 2013, **52**, 6160

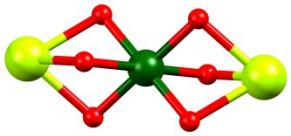
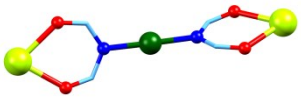
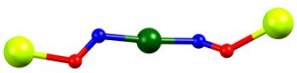
13		Gd, Tb, Dy	Single molecule magnet [NiTb]and [NiDy] U_{eff} [NiTb] = 14.4 K U_{eff} [NiDy] = 11.3 K Ferromagnetic [NiGd] J_{NiGd} = + 1.11 cm^{-1}	*Dalton Trans.*, 2013, **42**, 11227
		Gd, Tb, Ho, Er, Y	Ferromagnetic [NiGd] J_{NiGd} = + 1.38 cm^{-1}	
		Tb	Ferromagnetic	
14		Eu, Gd	Ferromagnetic [NiGd] J_{NiGd} = + 2.1 cm^{-1}	*Inorg. Chem.*, 2012, **51**, 5857
		Dy	Slow magnetic relaxation U_{eff} =9.2 K	
		Dy	Slow magnetic relaxation U_{eff} =10.1 K	

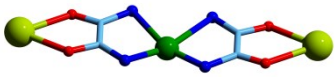
15		Ce, Dy	Antiferromagnetic [NiDy]	*Dalton Trans.*, 2012, **41**, 13755
16		Yb	Ferromagnetic [NiYb]	*Inorg. Chem.*, 2012, **51**, 11279
17		La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er	Slow magnetic relaxation [NiDy]	*Inorg. Chem.,* 2011, **50**, 5890
18		Dy	Single molecule magnet [NiDy]	*Inorg. Chem.*, 2011, **50**, 7268
19		Gd	Antiferromagnetic [NiGd] $J_{NiGd} = -0.22$ cm^{-1}	*Dalton Trans.*, 2010, **39**, 5020
20		Ce, Sm, Gd	Antiferromagnetic [NiCe], [NiSm]	*Inorg. Chem.*, 2010, **49**, 9012

21		Pr	Antiferromagnetic [NiPr]	*Eur. J. Inorg. Chem.*, 2010, 2768
22		Eu, Gd, Tb, Dy,	Ferromagnetic [NiGd], [NiTb], [NiDy]	*Inorg. Chem.*, 2008, **47**, 5736
23		Ce, Eu, Nd, Tb, Er	Antierromagnetic [NiCe], [NiEr] Ferromagnetic [NiNd], [NiTb]	*Inorg. Chem.*, 2005, **44**, 3524
24		Gd	Ferromagnetic [NiGd]	*Chem. Commun.*, 2004, 1048
25		Gd	Ferromagnetic [NiGd] $J_{NiGd} = +0.56\ cm^{-1}$	*Inorg. Chem.*, 2002, **41**, 605
26		La	–	*Inorg. Chem.*, 1999, **38**, 1351

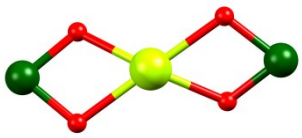
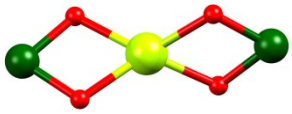
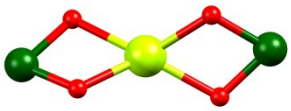
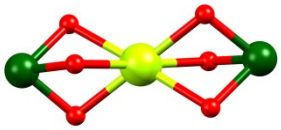
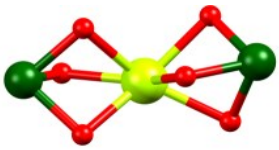
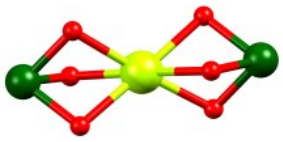
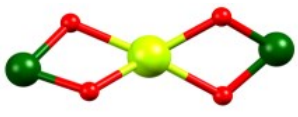
27		La	–	*Inorg. Chem.*, 1999, **38**, 1351
28	  	Sm, Er, Sm Yb	–	*Inorg. Chem.*, 1998, **37**, 4828
29		Dy	Antierromagnetic [NiDy]	*Chem. Eur. J.*, 1998, **4**, 1616
30		Gd	Ferromagnetic [NiGd]	*Inorg. Chem.*, 1997, **36**, 4284

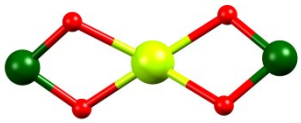
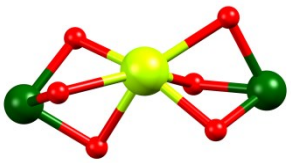
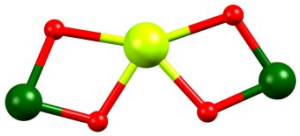
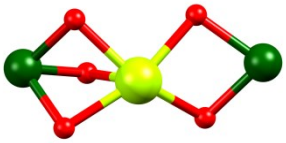
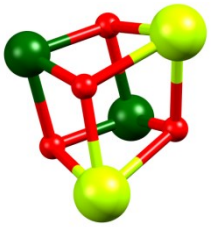
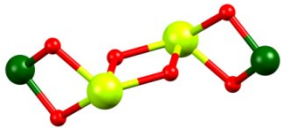
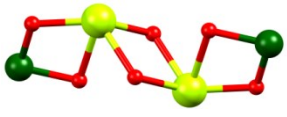
NiLn$_2$

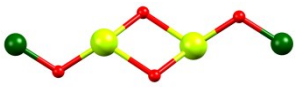
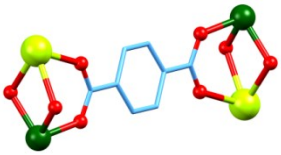
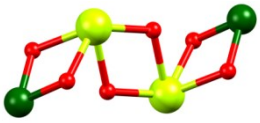
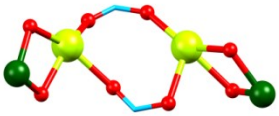
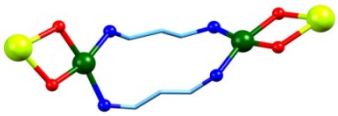
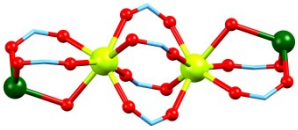
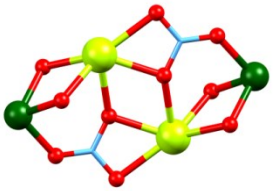
1		Dy	Single molecule magnet [NiDy$_2$]	*Inorg. Chem.*, 2015, **54**, 4337
2		Dy	Ferromagnetic [NiGd]	*Chem. Eur. J.*, 2007, **13**, 1602
3		La, Tb, Dy, Ho, Er	Single molecule magnet [NiDy$_2$]	Polyhedron, 2005, **24**, 2588

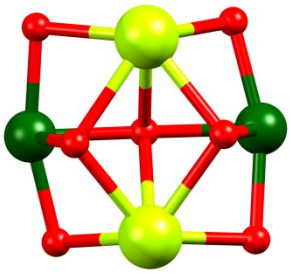
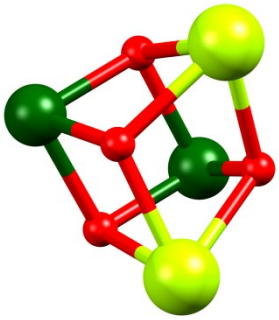
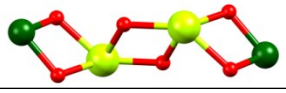
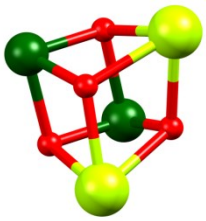
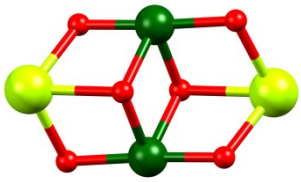
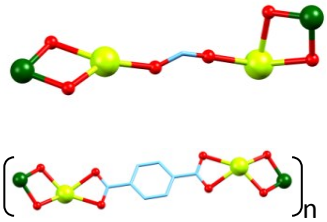
4		Yb, Lu	–	*J. Chem. Soc., Dalton Trans.*, 1998, 959

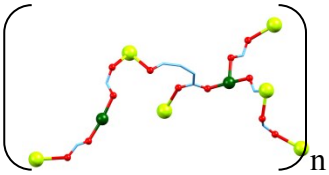
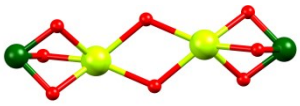
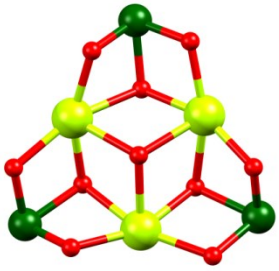
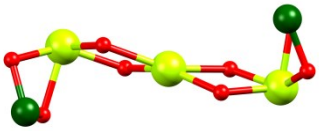
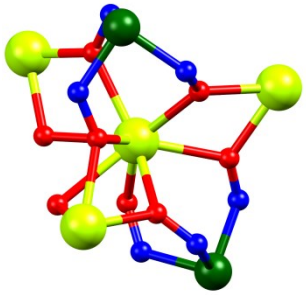
Ni_2Ln

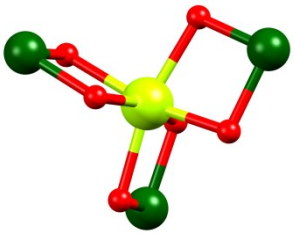
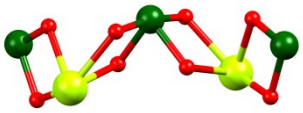
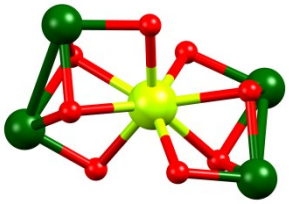
1		La	Antiferromagnetic [Ni_2La]	*Dalton Trans.*, 2014, **43**, 17375
2		Gd, Tb, Dy, Ho	Slow magnetic relaxation [Ni_2Dy]	*Chem. Asian J.*, 2014, **9**, 1876
3		Gd	Ferromagnetic [Ni_2Gd]	*Inorg. Chem.*, 2009, **48**, 5555
		Gd	Ferromagnetic [Ni_2Gd] $J_{NiGd} = +0.91$ cm^{-1}	
4		Gd, Yb	Ferromagnetic [Ni_2Ln]	*Inorg. Chem.*, 2008, **47**, 2280
5		La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er	Single molecule magnet [Ni_2Dy] $U_{eff} = 10.8$ K	*Inorg. Chem.*, 2008, **47**, 4918
6		Eu	–	*Eur. J. Inorg. Chem.*, 2008, 5235

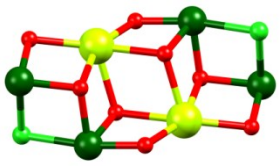
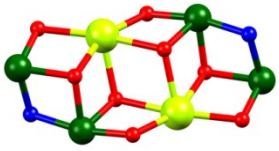
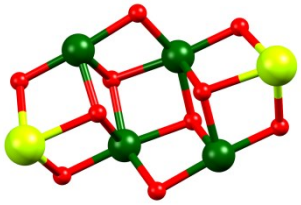
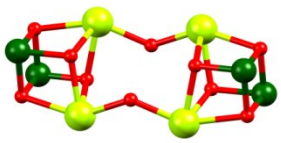
7		La–Lu except for Pm	Weakly antiferromagnetic [Ni_2Ce], [Ni_2Pr], and [Ni_2Nd] Ferromagnetic [Ni_2Gd], [Ni_2Tb], [Ni_2Dy], [Ni_2Ho], and [Ni_2Er].	*Inorg. Chem.*, 2007, **46**, 3492
8		Gd	Ferromagnetic [Ni_2Gd]	*Chem. Commun.*, 2004, 1048
9		Pr, Sm, Tb, Er, Lu	Ferromagnetic [Ni_2Gd], [Ni_2Tb], [Ni_2Er]	*Inorg. Chem.*, 2003, **42**, 1576
10		La, Dy, Yb	Antiferromagnetic [Ni_2Ln]	*Inorg. Chem.*, 2000, **39**, 508
		Ni_2Ln_2		
1		Gd, Tb, Dy, Ho	–	*New J. Chem.*, 2020, **44**, 4812
2		Tb, Dy, Ho, Er, Tm, Yb	Slow magnetic relaxation [Ni_2Tb_2] and [Ni_2Dy_2] U_{eff} [Ni_2Tb_2] =13.6 K U_{eff} [Ni_2Dy_2] = 11.52 K	*Dalton Trans.*, 2017, **46**, 12558
3		Gd, Dy, Y	Slow magnetic relaxation [Ni_2Dy_2] U_{eff}= 16.0 K	*Inorg. Chem.*, 2017, **56**, 11387

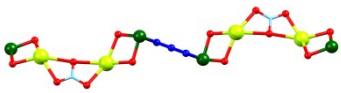
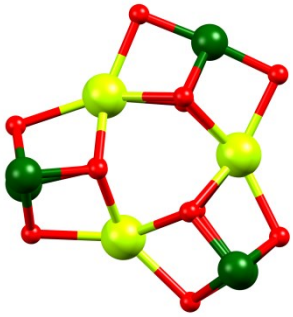
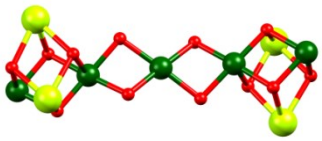
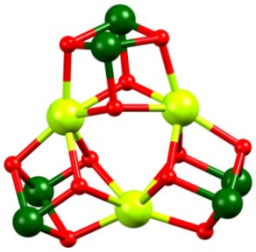
4		Dy	Single molecule magnet $[Ni_2Dy_2]$	*Chem. Eur. J.*, 2016, **22**, 18840
5		La, Gd, Tb, Dy	Ferromagnetic $[Ni_2Ln_2]$	*New J. Chem.*, 2016, **40**, 6998
6		Tb, Dy, Ho, Er, Tm, Yb, Lu	Ferromagnetic$[Ni_2Tb_2]$ and $[Ni_2Dy_2]$	Polyhedron, 2015, **85**, 697
7		Dy, Tb, Ho, Lu	Single molecule magnet $[Ni_2Dy_2]$ U_{eff} = 19.0 K	*Chem. Eur. J.*, 2014, **20**, 14235
8		Dy, Gd	Slow magnetic relaxation $[Ni_2Dy_2]$ U_{eff}= 7.4 K	*Inorg. Chem.*, 2014, **22**, 12092
9		La, Gd, Tb, Dy, Ho	Slow magnetic relaxation $[Ni_2Dy_2]$	*Inorg. Chem.*, 2014, **53**, 9785
10		Gd, Tb, Dy	Single molecule magnet $[Ni_2Tb_2]$ and $[Ni_2Dy_2]$ U_{eff} $[Ni_2Tb_2]$ =12.2 K/6.1 K U_{eff} $[Ni_2Dy_2]$ = 18.1 K/14.5 K	*Inorg. Chem.*, 2013, **52**, 7218
11		La, Gd, Tb, Dy	Antiferromagnetic $[Ni_2Dy_2]$	*Inorg. Chem.*, 2012, **51**, 10211

12		La, Tb, Dy	Antiferromagnetic $[Ni_2Ln_2]$	*Inorg. Chem.*, 2012, **51**, 10211
13		Gd, Dy	Weak ferromagnetic Ni···Ln interaction and weak antiferromagnetic Ln···Ln interaction	*Dalton Trans.*, 2012, **41**, 2320
14		Yb	–	*Inorg. Chem.*, 2011, **50**, 5890
15		Dy, Tb, Gd	Slow magnetic relaxation $[Ni_2Dy_2]$	*Inorg. Chem.*, 2011, **50**, 1304
16		Tb, Dy	Single molecule magnet $[Ni_2Dy_2]$ U_{eff} = 18–28 K	*Inorg. Chem.*, 2011, **50**, 11604
17		Dy	Single molecule magnet $[Ni_2Dy_2]$ U_{eff} = 13.6 K Single molecule magnet $[Ni_2Dy_2]_n$ U_{eff} = 17.4 K	*Dalton Trans.*, 2010, **39**, 4802

18		Gd	Antiferromagnetic [Ni_2Gd_2]	*Inorg. Chem.*, 2005, **44**, 5241
19		Gd	Ferromagnetic [Ni_2Gd_2]	*Chem. Commun.*, 2004, 1048
20		Er	Antiferromagnetic [Ni_2Er_2]	*J. Chem. Soc., Dalton Trans.*, 1997, 1665
Ni_2Ln_3				
1		Dy ,Tb, Gd, Ho, Er	Single molecule magnet [Ni_3Dy_3] U_{eff} = 10 K	*Inorg. Chem.*, 2014, **53**, 7815
2		Gd, Dy, Tb, Ho	Single molecule magnet [Ni_2Dy_3] U_{eff} = 85 K	*Inorg. Chem.*, 2013, **52**, 13078
Ni_2Ln_4				
1		Gd, Dy	Ferromagnetic [Ni_2Gd_4] Slow magnetic relaxation [Ni_2Dy_4]	*RSC Adv.*, 2014, **4**, 53870

Ni_3Ln				
1		Gd, Dy	Single molecule magnet $[Ni_3Dy]$	*Inorg. Chem.*, 2010, **49**, 9737
Ni_3Ln_2				
1		La, Ce, Eu	–	*ChemistryS elect*, 2017, **2**, 7865
Ni_4Ln				
1		Gd, Tb, Dy, Ho	Ferromagnetic $[Ni_4Ln]$ J_{NiGd} = + 0.34 cm^{-1} $[Ni_4Gd]$	*Eur. J. Inorg. Chem.*, 2014, 3393
Ni_4Ln_2				
1		Gd, Tb, Dy, Ho	Single molecule magnet $[Ni_4Tb_2]$, $[Ni_4Dy_2]$ and $[Ni_4Ho_2]$ U_{eff} $[Ni_4Tb_2]$ =13 K U_{eff} $[Ni_4Dy_2]$ = 20 K U_{eff} $[Ni_4Ho_2]$ = 19 K	*Cryst. Growth Des.*, 2020, **20**, 7300

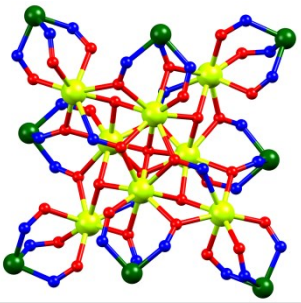
2	 	Dy, Tb, Ho	Single molecule magnet $[Ni_4Tb_2]$ and $[Ni_4Dy_2]$ U_{eff} $[Ni_4Tb_2]$ =26.3 K U_{eff} $[Ni_4Dy_2]$ = 23.0 K Single molecule magnet $[Ni_4Tb_2]$ and $[Ni_4Dy_2]$ U_{eff} $[Ni_4Tb_2]$ = 30.6 K U_{eff} $[Ni_4Dy_2]$ = 26.0 K	*Inorg. Chem.*, 2019, **58**, 12184
3		Gd, Tb, Dy, Ho	Single molecule magnet $[Ni_4Tb_2]$, $[Ni_4Dy_2]$ Slow magnetic relaxation $[Ni_4Ho_2]$	*Inorg. Chem.*, 2014, **53**, 3519
4		Gd, Dy	Antiferromagnetic $[Ni_4Gd_2]$ Slow magnetic relaxation $[Ni_4Dy_2]$	*Inorg. Chem.*, 2012, **51**, 2699
	Ni_4Ln_4			
1		Y, Gd, Tb, Dy, Ho, Er	Ferromagnetic $[Ni_4Ln_4]$ J_{NiGd} =+ 0.86 cm^{-1} $[Ni_4Gd_4]$	*ACS Omega*, 2018, **3**, 5202
2		Dy ,Tb, Gd, Ho	Single molecule magnet $[Ni_4Dy_4]$ Slow magnetic relaxation $[Ni_4Tb_4]$	*Inorg. Chem.*, 2016, **55**, 8422

3		Sm, Gd	Ferromagnetic [Ni_4Gd_4]	*Dalton Trans.*, 2014, **43**, 9136
		Ni_5Ln_3		
1		Gd, Dy	Ferromagnetic [Ni_5Gd_3] Slow magnetic relaxation [Ni_5Dy_3]	*Dalton Trans.*, 2013, **42**, 5298
		Ni_5Ln_4		
1		Eu, Gd, Dy	Single molecule magnet [Ni_5Dy_4] Ferromagnetic [Ni_5Gd_4] Ferromagnetic [Ni_5Eu_4]	*Dalton Trans.*, 2018, **47**, 16850
		Ni_6Ln_3		
1		Gd, Dy, Er	Single molecule magnet [Ni_6Dy_3] U_{eff} = 24 K Antiferromagnetic [Ni_6Er_3] Ferromagnetic [Ni_6Gd_3]	*Inorg. Chem.*, 2015, **54**, 7089

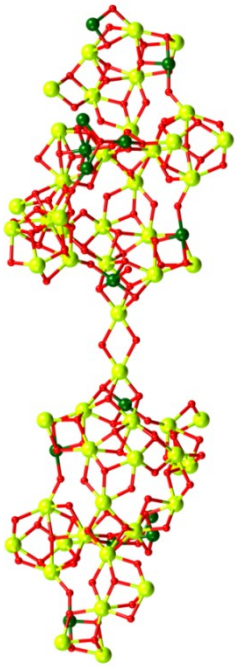
Ni_6Ln_6

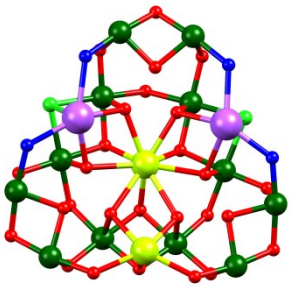
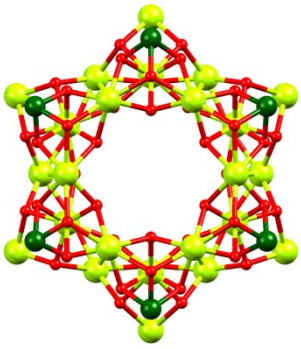
1		Gd, Dy	Ferromagnetic [Ni_6Gd_6]	*Angew. Chem.*, 2011, **123**, 3776

Ni_8Ln_8

1		Dy	Slow magnetic relaxation [Ni_8Dy_8]	*Inorg. Chem.*, 2010, **49**, 9743

Large nuclearity

1		Gd, Dy	Slow magnetic relaxation [$Ni_{10}Dy_{42}$]	*J. Am. Chem. Soc.*, 2012, **134**, 3314

2		Dy, Tb	Slow magnetic relaxation $[Na_2Ni_{12}Ln_2]$	*Chem. Commun.*, 2012, **48**, 7456
3		Gd	Antiferromagnetic $[Ni_{12}Gd_{36}]$	*Angew. Chem.*, 2011, **123**, 10837

Color code: Ni^{II}: Deep green, Ln^{III}: Light green, Na: Violet, Phosphorous: Orange, Oxygen: Red, Nitrogen: Blue, Chloride: Green

Table S2 Crystal refinement parameters of **A3** and complexes **1**–**4**.

Complex	**A3**	**1**	**2**	**3**	**4**
Chemical formula	$C_{28}H_{42}Cl_2N_4NiO_{14}$	$C_{30}H_{39}Gd_2N_9NiO_{18}$	$C_{30}H_{39}N_9NiO_{18}Tb_2$	$C_{30}H_{39}Dy_2N_9NiO_{18}$	$C_{30}H_{39}Ho_2N_9NiO_{18}$
Formula weight	788.25	1186.89	1190.27	1197.41	1202.27
Crystal color, habit	Orange block	Orange block	Orange block	Orange block	Orange block
Temperature (K)	296(2)	298(2)	297(2)	293(2)	296(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions					
a (Å)	11.4638(7)	12.8995(7)	12.8433(12)	12.8472(8)	12.8244(6)
b(Å)	12.0205(8)	18.7091(10)	18.6429(17)	18.6399(12)	18.6644(8)
c(Å)	14.4633(9)	18.0277(10)	17.9984(16)	17.9789(11)	17.9432(8)
β(deg)	68.567(2)	109.147(2)	108.867(4)	108.883(2)	108.793(2)
Volume ($Å^3$), Z	1798.5(2)	4110.1(4)	4077.9(7)	4073.7(4)	4065.9(3)
Density (mg m^{-3})	1.456	1.918	1.942	1.956	1.967
Absolute coefficient (mm^{-1})	0.757	3.727	3.973	4.173	4.398
F(000)	824.0	2328.0	2344.0	2352.0	2360.0
Crystal size (mm)	0.28×0.22×0.17	0.32×0.25×0.25	0.30×0.23×0.22	0.28×0.22×0.16	0.27×0.26×0.18

Complex	A3	1	2	3	4
θ range (deg)	1.514–24.997	2.484– 26.353	2.778– 26.094	2.492– 25.698	2.490– 25.714
Limiting indices	−13≤h≤13 −14≤k≤13 −17≤l≤17	−16≤h≤16 −23≤k≤23 −22≤l≤22	−15≤h≤15 −22≤k≤23 −22≤l≤22	−15≤h≤15 −22≤k≤22 −21≤l≤21	−15≤h≤15 −22≤k≤22 −21≤l≤21
Reflections collected	20941	59314	53741	55888	40778
Unique reflections (R_{int})	6335 (0.0244)	8394 (0.0226)	8086 (0.0365)	7755 (0.0217)	7759 (0.0484)
Reflections with I>2σ(I) Completeness to θ	5231 99.6 % (24.99)	7190 99.5 %(25.24)	6525 99.0 % (25.24)	6686 99.5 % (25.24)	5930 99.3 % (25.24)
Data/Resistant /Parameters	6310/76/451	8352/51/571	8003/34/569	7720/21/564	7704/52/571
GOOF on F^2	1.106	1.180	1.059	1.225	1.022
Final R indices [I > 2σ(I)]	0.0787[b], (0.2523[c])	0.0372[b], (0.0757[c])	0.0686[b], (0.1618[c])	0.0376[b], (0.0818[c])	0.0411[b], (0.0922[c])
R indices (all data)	0.0902[b], (0.2682[c])	0.0475[b], (0.0834[c])	0.0856[b], (0.1781[c])	0.0484[b], (0.0933[c])	0.0630[b], (0.1043[c])
Max/Min residual peaks (e $Å^{-3}$)	1.129/–0.593	1.510/–0.939	4.194/–1.799	1.598/–0.859	1.315/–1.053

[a]Graphite monochromator, [b]$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$

Table S3 Continuous Shape Measures (CShMs) of lanthanide (Gd, Tb, Dy and Ho) centers in complexes **1–4** relative to ideal 8/9−vertex polyhedra. The lowest CShMs value which corresponds to closest geometry is highlighted in bold.

8−vertex polyhedra						
	Gd1	**Tb1**	**Dy1**	**Ho1**	**Symmetry**	**Ideal shape**
OP–8	32.417	32.239	32.187	32.227	D_{8h}	Octagon
HPY–8	22.510	22.867	22.934	23.121	C_{7v}	Heptagonal pyramid
HBPY–8	16.233	16.407	16.424	16.529	D_{6h}	Hexagonal bipyramid
CU–8	12.284	12.135	12.063	11.900	*Oh*	Cube
SAPR–8	3.535	3.368	3.337	3.295	D_{4d}	Square antiprism
TDD–8	**1.415**	**1.356**	**1.290**	**1.240**	$\boldsymbol{D_{2d}}$	**Triangular dodecahedron**
JGBF–8	12.399	12.496	12.412	12.406	D_{2d}	Johnson gyrobifastigium J26
JETBPY–8	26.879	27.192	27.211	27.532	D_{3h}	Johnson elongated triangular bipyramid J14
JBTPR–8	2.488	2.474	2.401	2.410	C_{2v}	Biaugmented trigonal prism J50
BTPR–8	2.214	2.196	2.175	2.177	C_{2v}	Biaugmented trigonal prism
JSD–8	3.116	3.071	2.959	2.920	D_{2d}	Snub diphenoid J84
TT–8	12.658	12.494	12.412	12.242	*Td*	Triakis tetrahedron
ETBPY–8	23.810	24.093	24.219	24.295	D_{3h}	Elongated trigonal bipyramid
9−vertex polyhedra						
	Gd2	**Tb2**	**Dy2**	**Ho2**	**Symmetry**	**Ideal shape**
EP–9	33.396	33.646	33.630	33.888	D_{9h}	Enneagon
OPY–9	24.246	24.274	24.416	24.525	C_{8v}	Octagonal pyramid
HBPY–9	17.131	17.329	17.273	17.344	D_{7h}	Heptagonal bipyramid

JTC–9	12.029	12.148	12.223	12.268	C_{3v}	Johnson triangular cupola J3
JCCU–9	8.330	8.416	8.324	8.376	C_{4v}	Capped cube J8
CCU–9	6.938	7.039	6.938	6.995	C_{4v}	Spherical–relaxed capped cube
JCSAPR–9	4.408	4.403	4.278	4.233	C_{4v}	Capped square antiprism J10
CSAPR–9	3.364	3.360	3.249	3.220	C_{4v}	Spherical capped square antiprism
JTCTPR–9	3.888	3.860	3.768	3.747	D_{3h}	Tricapped trigonal prism J51
TCTPR–9	3.116	3.049	2.957	2.894	D_{3h}	Spherical tricapped trigonal prism
JTDIC–9	11.717	11.785	11.806	11.766	C_{3v}	Tridiminished icosahedron J63
HH–9	9.176	9.334	9.262	9.313	C_{2v}	Hula–hoop
MFF–9	**2.642**	**2.658**	**2.537**	**2.528**	$\boldsymbol{C_s}$	**Muffin**

Table S4 Some important metric parameter of Ln_2O_2 core.

Complex		1	2	3	4
Dihedral Angle	Angle between the Plane of O5−Ln1−O2 and O5−Ln2−O2	1.31(18)	1.2(4)	1.06(19)	1.0(3)
Torsional angle	O5−Ln2−O2−Ln1	1.13(13)	1.0(3)	0.91(13)	0.85(19)
Bridge angle	Ln1–O2–Ln2	108.57(16)	108.8(3)	108.62(16)	108.9(2)
	Ln1–O5–Ln2	108.52(16)	108.9(3)	108.68(17)	109.1(2)
Distance	Ln1–O1	2.418(3)	2.399(8)	2.387(4)	2.386(6)
	Ln1–O2	2.284(3)	2.271(7)	2.260(3)	2.251(4)
	Ln1–O4	2.474(3)	2.467(6)	2.458(3)	2.458(4)
	Ln1–O5	2.293(4)	2.269(8)	2.263(4)	2.244(5)
	Ln2–O2	2.286(3)	2.262(8)	2.259(4)	2.243(5)
	Ln2–O5	2.280(3)	2.260(6)	2.255(3)	2.243(4)
	Ln···Ln(intramolecular)	3.7108(6)	3.686(8)	3.670(6)	3.655(5)
	Ln···Ln(closest distance from packing)	7.4798(6)	7.4876(9)	7.4988(6)	7.5211(5)

Table S5 Hydrogen bonding parameter found in **1**–**4**, (distances, Å, angles, (˚)).

Complex 1				
Donor−H···Acceptor	**D–H**	**H···A**	**D···A**	**D–H···A**
O3···H3···O7A	0.85(6)	2.23(5)	3.048(6)	161(6)
O3···H3···O7B	0.85(6)	2.28(6)	2.959(7)	137(5)
O6···H6···O8A	0.86(4)	2.05(3)	2.874(9)	163(4)
Complex 2				
Donor−H···Acceptor	**D–H**	**H···A**	**D···A**	**D–H···A**
O3···H3···O7A	0.86(8)	2.27(8)	3.058(14)	153(8)
O3···H3···O7B	0.86(8)	2.18(8)	2.921(15)	144(8)
O6···H6···O8A	0.86(5)	2.10(5)	2.912(16)	158(5)
Complex 3				
Donor−H···Acceptor	**D–H**	**H···A**	**D···A**	**D–H···A**
O3···H3···O7A	0.85(7)	2.27(6)	3.088(7)	164(7)
O3···H3···O7B	0.85(7)	2.28(8)	2.926(8)	134(7)
O6···H6···O8A	0.86(4)	2.07(4)	2.895(9)	160(4)
Complex 4				
Donor−H···Acceptor	**D–H**	**H···A**	**D···A**	**D–H···A**
O3···H3···O7A	0.86(5)	2.36(5)	3.124(8)	147(5)
O3···H3···O7B	0.86(5)	2.16(5)	2.930(9)	148(6)
O6···H6···O8A	0.87(4)	2.04(3)	2.887(11)	165(5)

Table S6 C–H···π interaction parameter found in **1**–**4**, (distances, Å).

	H···π Distances (Å)			
C–H···π	**Complex 1**	**Complex 2**	**Complex 3**	**Complex 4**
C10–H10B···X	2.71	2.72	2.71	2.71
C23–H23A···Y	2.87	2.86	2.86	2.87
C28–H28A···Y	2.82	2.76	2.80	2.80

X = C1 – C6 inclusive, Y = Ni4 – N4 inclusive