Ferro- vs. antiferromagnetic exchange between two Ni(II) ions in a series of Schiff base heterometallic complexes: what makes the difference?

Olga Yu. Vassilyeva, Elena A. Buvaylo, Vladimir N. Kokozay, Brian W. Skelton, Alexandre N. Sobolev, Alina Bieńko and Andrew Ozarowski

Supplementary data

Table S1. Selected bond lengths [Å] and angles [°] for $[NiZnL'_2(OMe)Cl]_2$ (**1**) and $[NiZnL''(Dea)Cl]_2 \cdot 2DMF$ (**2**)

1		**2**	
Zn(1)–O(21)	2.000 (2)	Zn(1)–O(7)^2	1.9599(11)
Zn(1)–O(11)	2.0053 (19)	Zn(1)–O(11)	1.9901(11)
Zn(1)–O(1)	2.0980 (18)	Zn(1)–O(1)	2.0883(10)
Zn(1)–Cl(1)	2.2763 (8)	Zn(1)–Cl(1)	2.2106(5)
Zn(1)–O(12)	2.477 (2)	Zn(1)–O(17)	2.3674(11)
Ni(1)–O(11)	2.019 (2)	Ni(1)–O(11)	2.0212(10)
Ni(1)–O(21)^1	2.030 (2)	Ni(1)–N(10)	2.0364(13)
Ni(1)–N(26)^1	2.072 (3)	Ni(1)–O(1)	2.0736(10)
Ni(1)–N(16)	2.077 (3)	Ni(1)–O(1)^2	2.0850(10)
Ni(1)–O(1)^1	2.091 (2)	Ni(1)–O(7)	2.0940(11)
Ni(1)–O(1)	2.097 (2)	Ni(1)–N(4)	2.1126(13)
O(21)–Zn(1)–O(11)	99.04 (9)	O(7)^2–Zn(1)–O(11)	111.47(5)
O(21)–Zn(1)–O(1)	81.32 (8)	O(7)^2–Zn(1)–O(1)	85.63(4)
O(11)–Zn(1)–O(1)	80.23 (8)	O(11)–Zn(1)–O(1)	80.70(4)
O(21)–Zn(1)–Cl(1)	133.36 (6)	O(7)^2–Zn(1)–Cl(1)	120.55(4)
O(11)–Zn(1)–Cl(1)	127.59 (7)	O(11)–Zn(1)–Cl(1)	127.30(4)
O(1)–Zn(1)–Cl(1)	103.33 (6)	O(1)–Zn(1)–Cl(1)	109.90(3)
O(21)–Zn(1)–O(12)	110.21 (8)	O(7)^2–Zn(1)–O(17)	95.93(4)
O(11)–Zn(1)–O(12)	69.17 (7)	O(11)–Zn(1)–O(17)	71.78(4)
O(1)–Zn(1)–O(12)	148.45 (8)	O(1)–Zn(1)–O(17)	151.02(4)
Cl(1)–Zn(1)–O(12)	89.93 (5)	Cl(1)–Zn(1)–O(17)	94.24(4)
O(11)–Ni(1)–O(21)^1	174.91 (9)	O(11)–Ni(1)–N(10)	86.55(5)
O(11)–Ni(1)–N(26)^1	94.94 (10)	O(11)–Ni(1)–O(1)	80.34(4)
O(21)^1–Ni(1)–N(26)^1	89.26 (10)	N(10)–Ni(1)–O(1)	166.39(5)
O(11)–Ni(1)–N(16)	89.42 (9)	O(11)–Ni(1)–O(1)^2	95.44(4)
O(21)^1–Ni(1)–N(16)	93.08 (9)	N(10)–Ni(1)–O(1)^2	96.06(5)
N(26)^1–Ni(1)–N(16)	94.90 (11)	O(1)–Ni(1)–O(1)^2	81.67(4)
O(11)–Ni(1)–O(1)^1	94.59 (8)	O(11)–Ni(1)–O(7)	172.53(4)
O(21)^1–Ni(1)–O(1)^1	80.80 (8)	N(10)–Ni(1)–O(7)	86.56(5)
N(26)^1–Ni(1)–O(1)^1	166.71 (10)	O(1)–Ni(1)–O(7)	106.32(4)
N(16)–Ni(1)–O(1)^1	94.43 (10)	O(1)^2–Ni(1)–O(7)	82.41(4)
O(11)–Ni(1)–O(1)	79.96 (7)	O(11)–Ni(1)–N(4)	102.46(5)
O(21)^1–Ni(1)–O(1)	96.98 (8)	N(10)–Ni(1)–N(4)	103.94(5)
N(26)^1–Ni1–O(1)	93.11 (9)	O(1)–Ni(1)–N(4)	82.61(4)
N(16)–Ni(1)–O(1)	167.21 (10)	O(1)^2–Ni(1)–N(4)	153.77(4)
O(1)^1–Ni(1)–O(1)	79.47 (8)	O(7)–Ni(1)–N(4)	82.04(5)

Symmetry transformations used to generate equivalent atoms: ^{1} $-x+1/2, -y+3/2, -z+1$; ^{2} -x,1-y,1-z

Table S2. Selected bond lengths [Å] and angles [°] for $[Ni_2(H_3L''')_2(o\text{-Van})(MeOH)_2]Cl\cdot[ZnCl_2(H_4L''')(MeOH)]\cdot 2MeOH$ (**3**)

Ni(1)–O(11)	1.989(3)	Ni(2)–O(51)	2.065(3)
Ni(1)–N(10)	1.997(4)	Ni(2)–O(211)	2.085(3)
Ni(1)–O(31)	2.033(3)	Ni(2)–O(36)	2.153(3)
Ni(1)–O(321)	2.078(3)		
Ni(1)–O(41)	2.083(3)	Zn(3)–O(61)	1.966(3)
Ni(1)–O(111)	2.096(3)	Zn(3)–O(71)	2.078(4)
Ni(2)–O(21)	1.995(3)	Zn(3)–Cl(2)	2.2465(13)
Ni(2)–N(20)	2.000(4)	Zn(3)–Cl(1)	2.2558(13)
Ni(2)–O(31)	2.043(3)	Zn(3)–O(66)	2.425(3)
O(11)–Ni(1)–N(10)	95.19(14)	O(31)–Ni(2)–O(51)	92.70(12)
O(11)–Ni(1)–O(31)	92.56(12)	O(21)–Ni(2)–O(211)	174.41(12)
N(10)–Ni(1)–O(31)	171.32(14)	N(20)–Ni(2)–O(211)	81.24(13)
O(11)–Ni(1)–O(321)	91.43(12)	O(31)–Ni(2)–O(211)	88.94(12)
N(10)–Ni(1)–O(321)	87.70(13)	O(51)–Ni(2)–O(211)	88.28(12)
O(31)–Ni(1)–O(321)	88.20(12)	O(21)–Ni(2)–O(36)	90.26(12)
O(11)–Ni(1)–O(41)	92.61(12)	N(20)–Ni(2)–O(36)	97.64(13)
N(10)–Ni(1)–O(41)	93.21(13)	O(31)–Ni(2)–O(36)	76.28(11)
O(31)–Ni(1)–O(41)	90.34(12)	O(51)–Ni(2)–O(36)	168.62(12)
O(321)–Ni(1)–O(41)	175.77(13)	O(211)–Ni(2)–O(36)	88.65(12)
O(11)–Ni(1)–O(111)	176.34(12)	O(61)–Zn(3)–O(71)	86.52(13)
N(10)–Ni(1)–O(111)	81.51(14)	O(61)–Zn(3)–Cl(2)	118.11(11)
O(31)–Ni(1)–O(111)	90.84(12)	O(71)–Zn(3)–Cl(2)	101.10(15)
O(321)-Ni(1)–O(111)	90.03(12)	O(61)–Zn(3)–Cl(1)	125.60(11)
O(41)–Ni(1)–O(111)	86.02(12)	O(71)–Zn(3)–Cl(1)	98.97(14)
O(21)–Ni(2)–N(20)	93.48(13)	Cl(2)–Zn(3)–Cl(1)	113.75(5)
O(21)–Ni(2)–O(31)	96.13(12)	O(61)–Zn(3)–O(66)	72.28(12)
N(20)–Ni(2)–O(31)	168.62(13)	O(71)–Zn(3)–O(66)	157.53(13)
O(21)–Ni(2)–O(51)	93.82(12)	Cl(2)–Zn(3)–O(66)	95.55(9)
N(20)–Ni(2)–O(51)	92.72(13)	Cl(1)–Zn(3)–O(66)	87.86(9)

Table S3. Geometry of hydrogen bonds for **3** (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(113)-H(113)...Cl(3)	0.84(2)	2.21(2)	3.047(4)	176(6)
N(60)-H(60N)...O(61)	0.881(19)	1.97(4)	2.620(5)	130(4)
O(612)-H(612)...O(213)	0.83(2)	1.90(2)	2.717(5)	170(7)
O(71)-H(71)...O(611)	0.84(2)	1.84(3)	2.666(5)	166(8)
O(111)-H(111)...O(91)	0.84(2)	1.84(2)	2.666(4)	168(6)
O(112)-H(112)...O(11)[1]	0.83(2)	1.95(3)	2.762(4)	166(6)
O(211)-H(211)...O(112)[2]	0.84(2)	1.77(2)	2.605(4)	169(6)
O(212)-H(212)...Cl(3)[3]	0.84(2)	2.24(2)	3.069(4)	168(6)
O(213)-H(213)...Cl(1)[4]	0.84(2)	2.35(2)	3.180(3)	171(6)
O(41)-H(41)...O(21)	0.83(2)	1.86(2)	2.676(4)	167(3)

O(51)-H(51)...O(11)	0.81(2)	1.89(3)	2.664(4)	160(5)
O(611)-H(611)...O(81)[4]	0.84(2)	1.82(2)	2.645(5)	170(6)
O(613)-H(613)...Cl(3)[5]	0.85(2)	2.23(3)	3.064(4)	167(6)
O(81)-H(81)...Cl(2)	0.84(2)	2.27(2)	3.108(4)	171(6)
O(91)-H(91)...O(21)	0.84(2)	2.04(3)	2.850(4)	163(6)
O(112)-H(112)...O(16)[1]	0.83(2)	2.58(5)	3.130(5)	125(5)
O(51)-H(51)...O(16)	0.81(2)	2.59(4)	3.185(4)	131(4)

Symmetry transformations used to generate equivalent atoms: [1] -x,y+1/2,-z+3/2; [2] -x,y-1/2,-z+3/2; [3] x,y-1,z; [4] -x+1,y-1/2,-z+3/2; [5] -x+1,-y+1,-z+2.

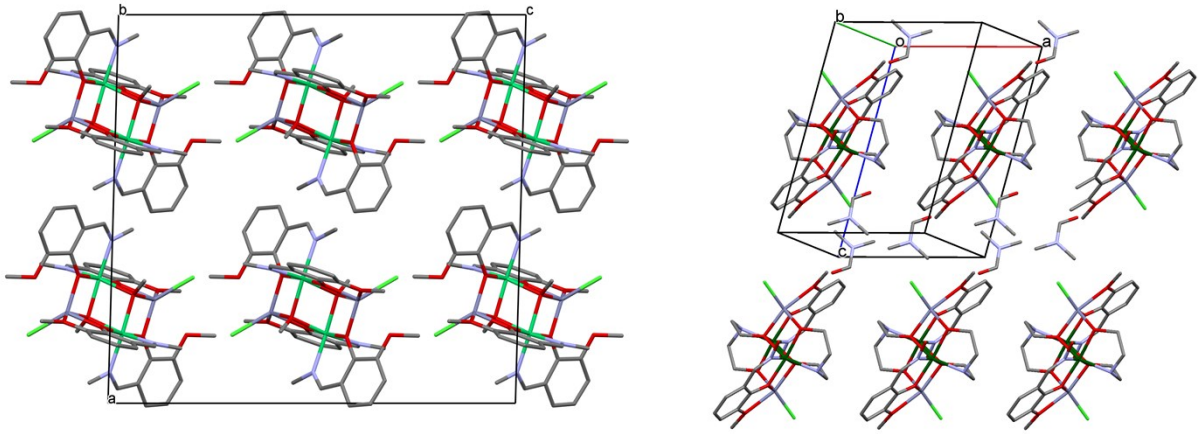

Figure S1. Fragments of crystal packing of $[NiZnL'_2(OMe)Cl]_2$ (**1**, left) and $[NiZnL''(Dea)Cl]_2 \cdot 2DMF$ (**2**, right). CH hydrogen atoms are omitted for clarity.

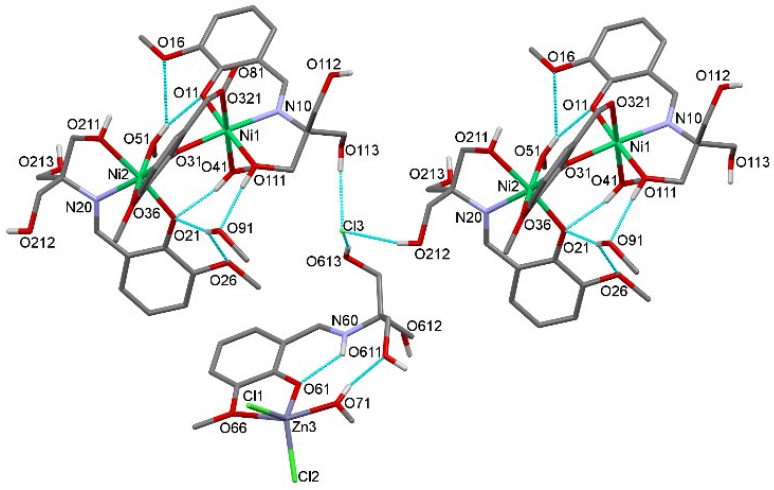

Figure S2. Fragment of the crystal structure of **3** showing the hydrogen bonding environment of the chloride anion Cl3. CH hydrogen atoms are omitted for clarity, H-bonds are shown as blue dotted lines.

Table S4. Results of magnetic data fitting

Complex	**1**	**2**	**3**
$g_{average}$	2.11(5)	2.23(2)	2.28(2)
J (cm^{-1})	7.7(1)	-6.5(1)	-0.6(2)
D_{Ni}*(cm^{-1})	2.27	-4.491	-11.398
E_{Ni}*(cm^{-1})	0.243	-0.684	-1.151
D_{12}*(cm^{-1})	-0.02	0.034	0**
E_{12}*(cm^{-1})	0.04	-0.06	0**
Monomer fraction	0.18	0**	0**
zJ (cm^{-1})	0.07	0.066	-1.1(2)

*Fixed as obtained from EPR. **Fixed.

Note that energies in Tables S5-S7 do not include the spin-orbit coupling contribution.

Table S5. Contributions of the ligand-field states to the ZFS in **1**.

Parent Term (O_h)	Energy (cm^{-1})	D (cm^{-1})	E(cm^{-1})
$^3T_{2g}(^3F)$	$^3B_2$ 7842	13.385	-10.062
	$^3B_3$ 7905	11.544	17.661
	$^3B_1$ 8009	-23.483	-7.359
$^3T_{1g}(^3F)$	13366	0.005	0.004
	13583	0.003	-0.003
	13860	0.002	-0.001
$^1E_g(^1D)$	18523	-0.000	0.000
	18576	-0.000	0.000
$^1T_{2g}(^1D)$	25586	-7.282	-7.304
	25634	-7.270	7.292
	25737	14.384	-0.005
$^3T_{1g}(^3P)$	29067	0.000	-0.000
	29175	0.000	-0.000
	29349	0.000	0.000
$^1A_{1g}(^1G)$	29626	0.005	0.000
$^1T_{1g}(^1G)$	32389	-0.003	0.003
	32468	-0.004	-0.004
	32605	-0.004	0.004
$^1E_g(^1G)$	37646	-0.010	0.009
	37706	-0.003	0.002
$^1T_{2g}(^1G)$	38273	0.794	-0.141
	38422	-0.288	0.460
	38472	-0.488	-0.338
$^1A_{1g}(^1S)$	71680	0.000	0.000

Table S6. Contributions of the ligand-field states to the ZFS in **2**

Parent Term (O_h)	Energy (cm^{-1})	D (cm^{-1})	E(cm^{-1})
$^3T_{2g}(^3F)$	$^3B_1$ 6802	-47.001	-4.604
	$^3B_2$ 7571	13.555	-4.040
	$^3B_3$ 7875	24.245	7.631
$^3T_{1g}(^3F)$	12295	0.067	-0.062
	12492	0.032	-0.031
	13730	0.032	-0.007
$^1E_g(^1D)$	18360	0.008	-0.000
	18444	-0.001	-0.001
$^1T_{2g}(^1D)$	24490	15.188	-0.018
	25109	-7.152	6.573
	25476	-7.144	-6.545
$^3T_{1g}(^3P)$	27830	0.002	0.000
	28614	0.003	-0.003
	29131	-0.000	-0.000
$^1A_{1g}(^1G)$	29445	-0.001	0.004
$^1T_{1g}(^1G)$	31406	-0.028	0.029
	32158	-0.026	-0.029
	32367	-0.058	0.051
$^1E_g(^1G)$	36542	-0.004	0.003
	36967	-0.101	-0.057
$^1T_{2g}(^1G)$	37319	-0.727	0.180
	37600	0.356	-0.158
	37746	0.389	0.043
$^1A_{1g}(^1S)$	70918	0.000	-0.000

Table S7. Contributions of the ligand-field states to the ZFS in **3**

Parent Term (O_h)	Energy (cm^{-1})	D (cm^{-1})	E(cm^{-1})
$^3T_{2g}(^3F)$	$^3B_1$ 6612	-64.799	-0.086
	$^3B_2$ 7806	26.750	-25.274
	$^3B_3$ 8848	24.099	22.153
$^3T_{1g}(^3F)$	13028	0.117	0.059
	13514	0.219	-0.177
	13902	-0.064	0.003
$^1E_g(^1D)$	18102	0.006	-0.000
	18582	0.000	-0.000
$^1T_{2g}(^1D)$	24446	15.680	0.003
	25423	-7.119	6.813
	26483	-6.753	-6.442
$^3T_{1g}(^3P)$	28322	0.005	0.004
	29212	0.011	-0.010
	29859	-0.005	-0.002
$^1A_{1g}(^1G)$	29976	0.000	0.001
$^1T_{1g}(^1G)$	31319	-0.052	-0.043
	32743	-0.092	0.090
	33440	0.028	-0.000
$^1T_{2g}(^1G)$	37320	0.081	-0.005
	37640	-0.028	0.020
	37966	-0.448	-0.012
$^1E_g(^1G)$	38401	0.776	0.109
	38563	-0.831	-0.210
$^1A_{1g}(^1S)$	71630	0.000	0.000

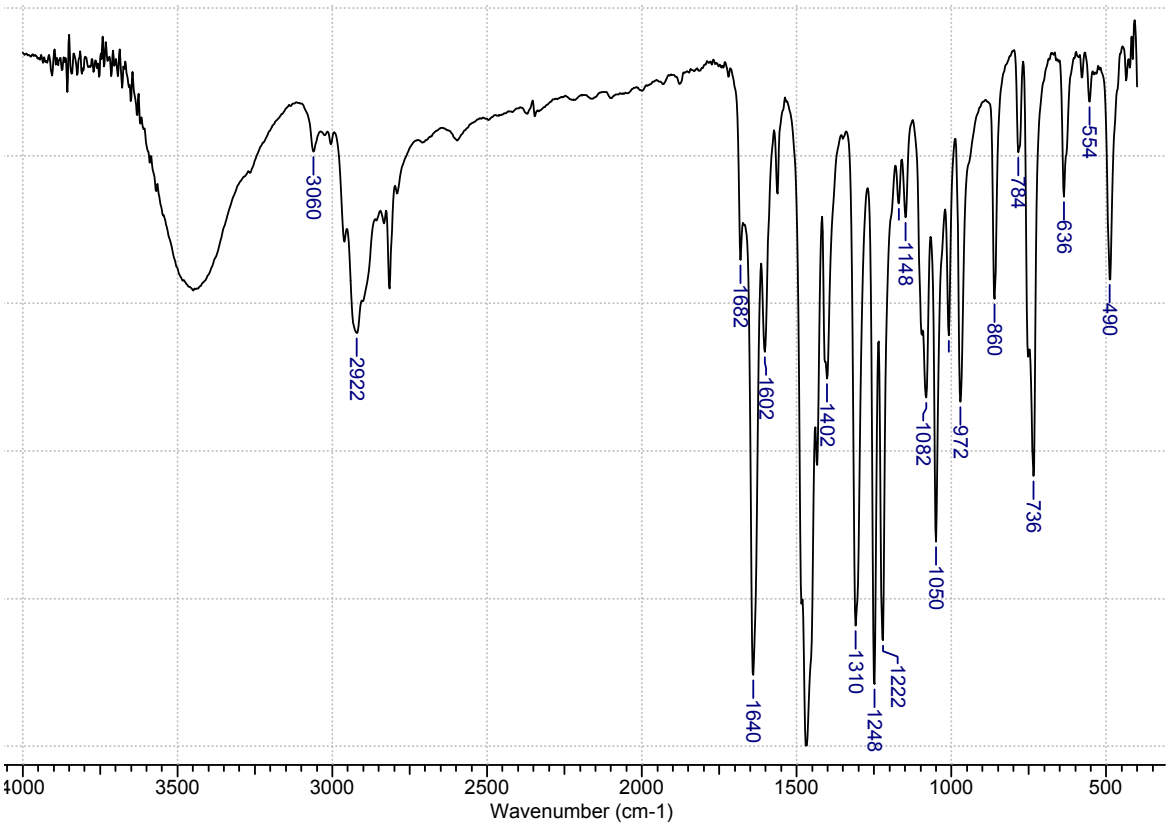

Figure S3. IR spectrum of $[NiZnL'_2(OMe)Cl]_2$ (**1**).

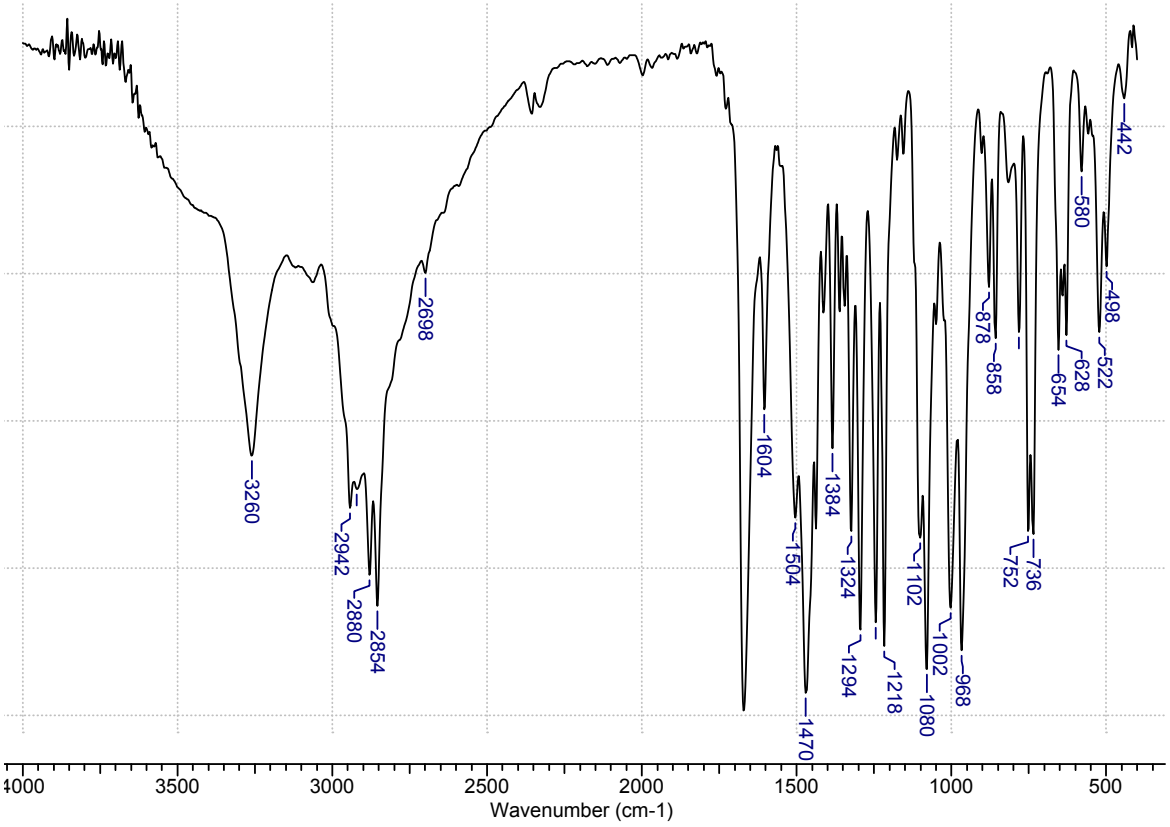

Figure S4. IR spectrum of $[NiZnL''(Dea)Cl]_2 \cdot 2DMF$ (**2**).

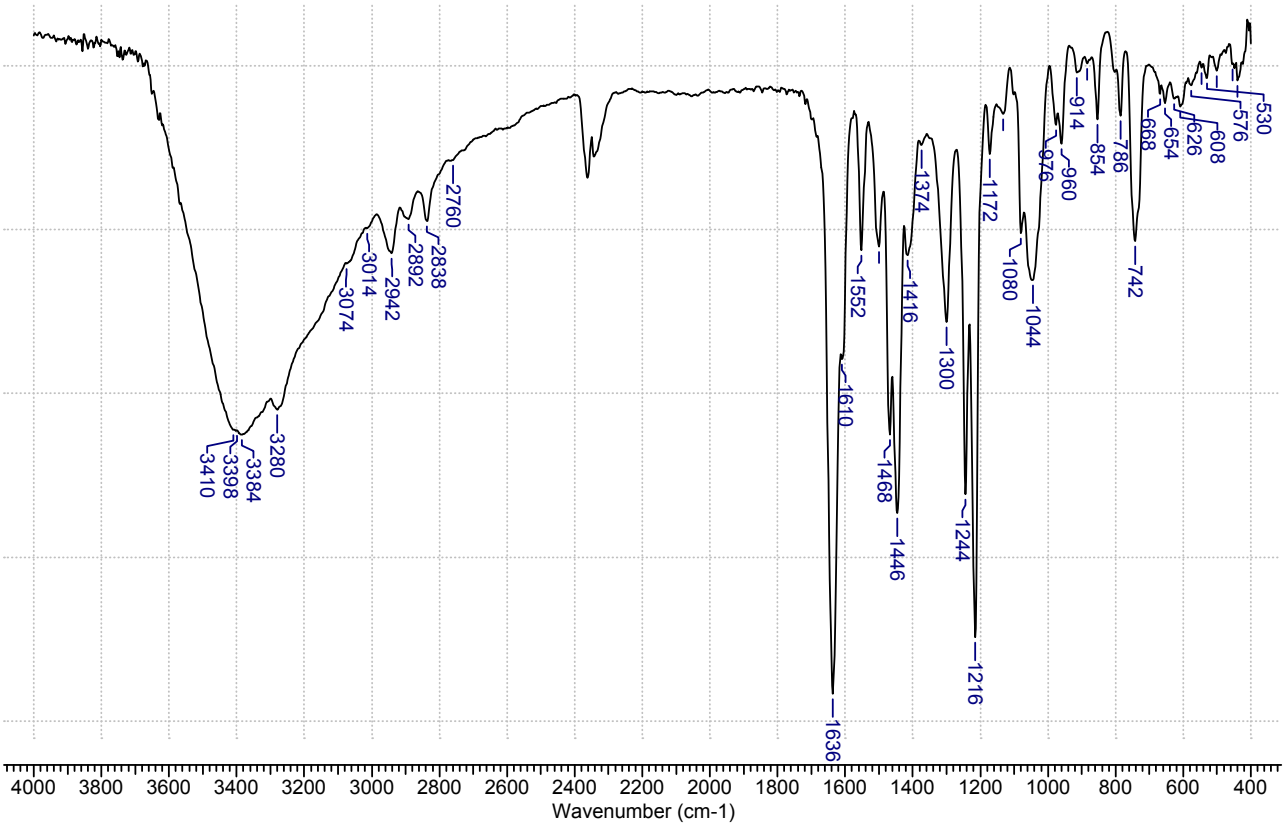

Figure S5. IR spectrum of $[Ni_2(H_3L''')_2(o\text{-Van})(MeOH)_2]Cl\cdot[ZnCl_2(H_4L''')(MeOH)]\cdot 2MeOH$ (**3**).

Table S8. Crystallographic data for **1**–**3**

	1	**2**	**3**
Empirical Formula	$C_{38}H_{46}Cl_2N_4Ni_2O_{10}Zn_2$	$C_{30}H_{48}Cl_2N_6Ni_2O_{12}Zn_2$	$C_{49}H_{76}Cl_3N_3Ni_2O_{23}Zn$
Formula weight	1037.85	1003.80	1364.26
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
T/K	100(2)	180(2)	100(2)
a/Å	19.6732 (5)	8.9536(4)	17.7587(3)
b/Å	10.9932 (2)	9.8327(4)	14.0514(2)
c/Å	20.6092 (3)	13.4081(5)	24.0434(4)
α/°	90	99.742(3)	90
β/°	91.555 (2)	104.655(4)	98.607(2)
γ/°	90	113.637(4)	90
Z	4	1	4
V/Å^3	4455.54 (15)	996.23(7)	5932.09(17)
D_{cal}/g cm^{-3}	1.547	1.673	1.528
No. of reflections measured	20435	29860	57005
No. of independent reflections	3977	10146	10579

R_{int}	0.0385	0.0357	0.0704
Absorption correction	Semi-empirical from equivalents	Analytical	Analytical
Data / restraints / parameters	3977/0/267	10146 / 0 / 248	10579 / 16 / 795
Goodness-of-fit on F^2	1.002	1.023	1.127
Final R_1 values ($I>2\sigma(I)$)	0.0403	0.0376	0.0555
Final w$R(F^2)$ values ($I>2\sigma(I)$)	0.1127	0.0845	0.1508
Final R_1 values (all data)	0.0463	0.0592	0.0734
Final w$R(F^2)$ values (all data)	0.1179	0.0955	0.1627
Largest diff. peak and hole/ e Å^{-3}	1.34 / −0.36	0.796 / −0.624	1.587 / -0.414
CCDC No.	1898551	1898552	1837991

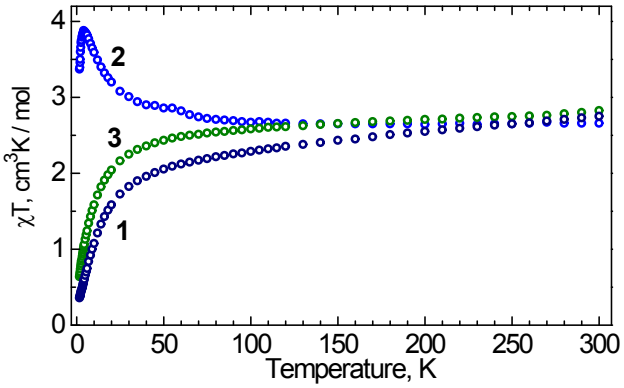

Figure S6. The original magnetic data. To obtain the plots in Figure 11 (main text), TIP per one Ni^{2+} of $950\cdot10^{-6}$ cgs emu, $250\cdot10^{-6}$ cgs emu and $300\cdot10^{-6}$ cgs emu was subtracted from data of **1**, **2** and **3**, respectively.