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Electronic Supporting Information

Two isostructural complexes of Ni(II) and Zn(II) with violurate and pyridine: A detailed structural, theoretical, magnetic, and NMR investigation

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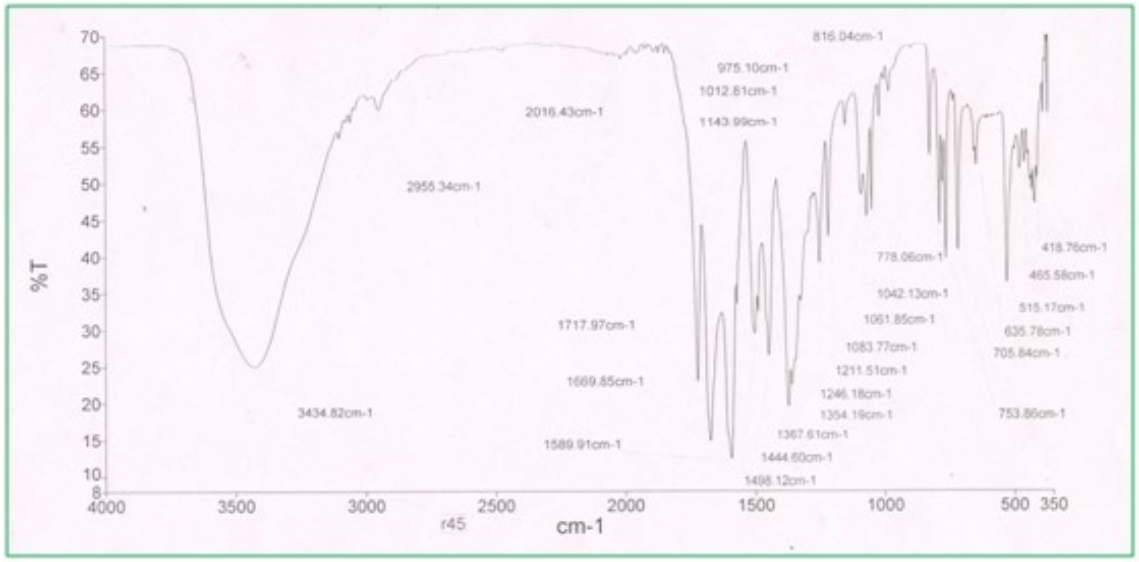

Fig. S1 IR Spectrum of $[Ni(dmv)_2(py)_2]\cdot 3H_2O$ (**1**)

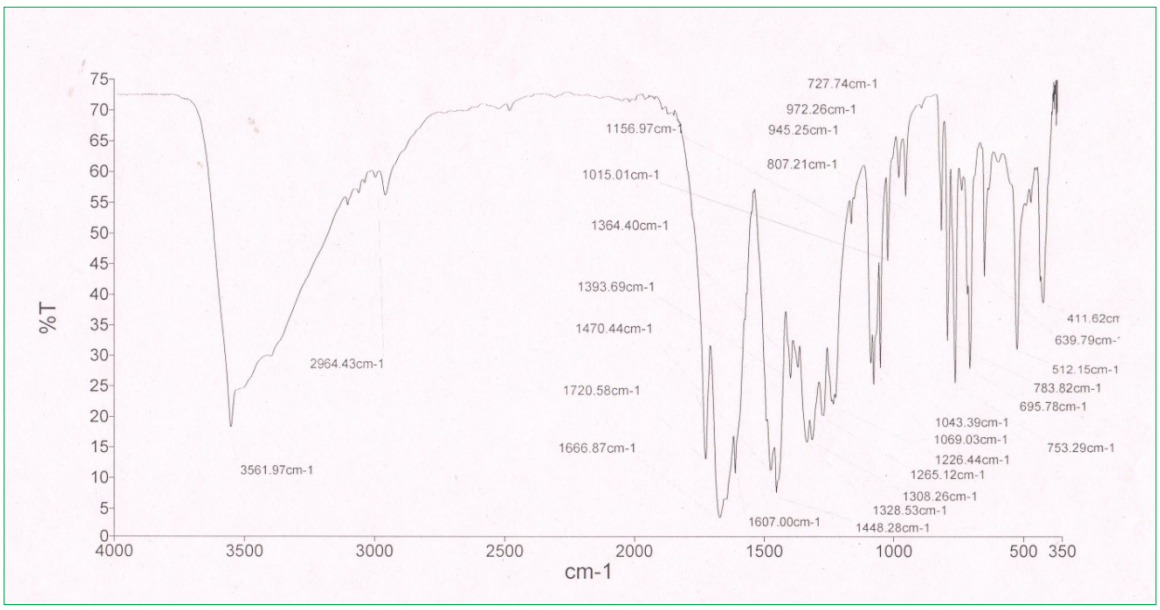

Fig. S2 IR Spectrum of $[Zn(dmv)_2(py)_2]\cdot 3H_2O$ (**2**)

Table S1 Crystal data and structure refinement for the complexes

Identification code	Complex **1**	Complex **2**
Empirical formula	$C_{22}H_{28}N_8NiO_{11}$	$C_{22}H_{28}N_8O_{11}Zn$
Formula weight	639.23	645.89
Temperature/K	100(2)	123(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.9490(5)	11.1064(9)
b/Å	11.9806(7)	12.1528(11)
c/Å	12.0973(6)	12.3032(12)
α/°	112.946(5)	113.663(9)
β/°	106.988(4)	106.663(8)
γ/°	99.066(4)	98.980(7)
Volume/Å^3	1329.48(13)	1385.8(2)
Z	2	2
ρ_{calc}g/cm^3	1.597	1.548
μ/mm^{-1}	1.728	0.959
F(000)	664.0	668.0
Crystal size/mm^3	0.3 × 0.23 × 0.16	0.21 × 0.18 × 0.13
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2θ range for data collection/°	8.878 to 145.25	6.916 to 67.702
Index ranges	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -14 ≤ l ≤ 12	-16 ≤ h ≤ 11, -18 ≤ k ≤ 17, -19 ≤ l ≤ 16
Reflections collected	7951	11499
Independent reflections	5070 [R_{int} = 0.0217, R_{sigma} = 0.0356]	9459 [R_{int} = 0.0285, R_{sigma} = 0.0822]
Data/restraints/parameters	5070/54/458	9459/35/427
Goodness-of-fit on F^2	1.046	1.016
Final R indexes [I≥ 2σ (I)]	R_1 = 0.0326, wR_2 = 0.0824	R_1 = 0.0638, wR_2 = 0.1304
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.0861	R_1 = 0.1111, wR_2 = 0.1583
Largest diff. peak/hole / e Å^{-3}	0.32/-0.35	0.78/-0.50

Table S2 Bond Lengths for **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O11	2.0551(11)	C43	C44	1.389(3)
Ni1	N11	2.0769(14)	C44	C45	1.385(2)
Ni1	N31	2.0707(14)	O21	C21	1.247(2)
Ni1	N41	2.0809(14)	O23	C22	1.213(2)
Ni1	O21	2.0709(13)	O24	C23	1.219(2)
Ni1	N21	2.0832(15)	N22	C21	1.365(2)
Ni1	O21A	1.86(3)	N22	C22	1.392(2)
Ni1	O22A	2.12(3)	N22	C25	1.474(2)
O11	C11	1.247(2)	N23	C22	1.387(2)
O12	N11	1.2601(17)	N23	C23	1.414(2)
O13	C12	1.213(2)	N23	C26	1.472(2)
O14	C13	1.219(2)	C21	C24	1.442(2)
N11	C14	1.345(2)	C23	C24	1.440(2)
N12	C11	1.365(2)	C24	N21	1.358(2)
N12	C12	1.399(2)	O22	N21	1.2478(19)
N12	C15	1.470(2)	O21A	C21A	1.260(17)
N13	C12	1.383(2)	O23A	C22A	1.214(17)
N13	C13	1.397(2)	O24A	C23A	1.221(17)
N13	C16	1.472(2)	N22A	C21A	1.382(16)
N31	C31	1.349(2)	N22A	C22A	1.396(17)
N31	C35	1.344(2)	N22A	C25A	1.478(18)
N41	C41	1.348(2)	N23A	C22A	1.391(17)
N41	C45	1.342(2)	N23A	C23A	1.404(16)
C11	C14	1.441(2)	N23A	C26A	1.475(18)
C13	C14	1.454(2)	C21A	C24A	1.419(17)
C31	C32	1.385(2)	C23A	C24A	1.431(16)
C32	C33	1.383(2)	C24A	N21A	1.39(2)
C33	C34	1.387(2)	O22A	N21A	1.247(10)
C34	C35	1.382(2)	O3WA	O3WA[1]	1.731(10)
C41	C42	1.380(2)	O3WB	O3WC	1.37(3)
C42	C43	1.382(2)			

[1]2-X,-Y,1-Z

Table S3 Bond Angles for **1**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O11	Ni1	N11	79.27(5)	C33	C32	C31	119.30(15)
O11	Ni1	N31	93.83(5)	C32	C33	C34	118.57(16)
O11	Ni1	N41	89.24(5)	C35	C34	C33	119.00(16)
O11	Ni1	O21	170.36(5)	N31	C35	C34	122.85(15)
O11	Ni1	N21	100.81(5)	N41	C41	C42	122.50(15)
O11	Ni1	O22A	80.4(6)	C41	C42	C43	119.07(16)
N11	Ni1	N41	91.48(5)	C42	C43	C44	118.96(16)
N11	Ni1	N21	85.29(6)	C45	C44	C43	118.66(16)
N11	Ni1	O22A	94.4(7)	N41	C45	C44	122.62(16)
N31	Ni1	N11	172.64(5)	C21	O21	Ni1	110.64(11)
N31	Ni1	N41	90.97(5)	C21	N22	C22	123.35(15)
N31	Ni1	O21	95.81(5)	C21	N22	C25	119.54(15)
N31	Ni1	N21	93.59(5)	C22	N22	C25	117.00(14)
N31	Ni1	O22A	81.8(7)	C22	N23	C23	125.25(15)
N41	Ni1	N21	168.64(5)	C22	N23	C26	116.42(15)
N41	Ni1	O22A	166.9(5)	C23	N23	C26	118.32(16)
O21	Ni1	N11	91.10(5)	O21	C21	N22	120.19(16)
O21	Ni1	N41	90.70(5)	O21	C21	C24	121.72(15)
O21	Ni1	N21	78.50(5)	N22	C21	C24	118.06(15)
O21A	Ni1	O11	168.0(8)	O23	C22	N22	121.14(17)
O21A	Ni1	N11	94.8(10)	O23	C22	N23	121.97(17)
O21A	Ni1	N31	91.5(11)	N23	C22	N22	116.89(15)
O21A	Ni1	N41	101.4(8)	O24	C23	N23	119.78(16)
O21A	Ni1	O22A	89.8(10)	O24	C23	C24	126.00(16)
C11	O11	Ni1	111.93(10)	N23	C23	C24	114.20(15)
O12	N11	Ni1	124.91(11)	C23	C24	C21	121.36(15)
O12	N11	C14	121.92(14)	N21	C24	C21	112.59(14)
C14	N11	Ni1	113.17(10)	N21	C24	C23	125.95(16)
C11	N12	C12	123.56(13)	C24	N21	Ni1	111.61(11)
C11	N12	C15	119.01(14)	O22	N21	Ni1	125.97(11)
C12	N12	C15	117.33(13)	O22	N21	C24	121.75(14)
C12	N13	C13	125.59(14)	C21A	O21A	Ni1	118(2)
C12	N13	C16	116.78(14)	C21A	N22A	C22A	122.9(17)
C13	N13	C16	117.55(14)	C21A	N22A	C25A	122.7(19)
C31	N31	Ni1	121.60(11)	C22A	N22A	C25A	114.3(19)
C35	N31	Ni1	120.46(11)	C22A	N23A	C23A	122.8(18)
C35	N31	C31	117.89(14)	C22A	N23A	C26A	115.4(19)
C41	N41	Ni1	120.46(11)	C23A	N23A	C26A	121.5(19)
C45	N41	Ni1	121.20(11)	O21A	C21A	N22A	114.0(17)
C45	N41	C41	118.17(14)	O21A	C21A	C24A	129(2)
O11	C11	N12	119.68(14)	N22A	C21A	C24A	115.8(17)
O11	C11	C14	122.57(14)	O23A	C22A	N22A	120(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N12	C11	C14	117.74(14)	O23A	C22A	N23A	121(2)
O13	C12	N12	120.75(15)	N23A	C22A	N22A	117.7(17)
O13	C12	N13	122.21(16)	O24A	C23A	N23A	121.2(18)
N13	C12	N12	117.03(14)	O24A	C23A	C24A	123.4(17)
O14	C13	N13	120.45(15)	N23A	C23A	C24A	115.0(17)
O14	C13	C14	125.28(15)	C21A	C24A	C23A	122.9(18)
N13	C13	C14	114.25(14)	N21A	C24A	C21A	118.9(13)
N11	C14	C11	112.49(14)	N21A	C24A	C23A	117.7(13)
N11	C14	C13	126.12(14)	N21A	O22A	Ni1	118.2(19)
C11	C14	C13	121.38(14)	O22A	N21A	C24A	129.2(19)
N31	C31	C32	122.37(16)				

Table S4 Bond Lengths for **2**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	N11	2.203(3)	N13A	C13A	1.409(14)
Zn1	O11	2.155(3)	N13A	C16A	1.475(15)
Zn1	O12A	2.164(14)	C11A	C14A	1.430(15)
Zn1	O11A	1.959(14)	C13A	C14A	1.425(15)
Zn1	O21	2.0972(17)	O21	C21	1.249(3)
Zn1	N21	2.182(2)	O22	N21	1.264(2)
Zn1	N31	2.087(2)	O23	C22	1.214(3)
Zn1	N41	2.133(2)	O24	C23	1.217(3)
O12	N11	1.255(4)	N21	C24	1.343(3)
N11	C14	1.343(4)	N22	C21	1.360(3)
O11	C11	1.248(4)	N22	C22	1.386(4)
O13	C12	1.209(4)	N22	C25	1.467(3)
O14	C13	1.214(4)	N23	C22	1.383(4)
N12	C11	1.374(4)	N23	C23	1.395(3)
N12	C12	1.386(4)	N23	C26	1.466(4)
N12	C15	1.463(5)	C21	C24	1.441(3)
N13	C12	1.373(5)	C23	C24	1.431(4)
N13	C13	1.413(4)	N31	C32	1.347(3)
N13	C16	1.473(5)	N31	C36	1.334(4)
C11	C14	1.434(5)	C32	C33	1.379(4)
C13	C14	1.433(4)	C33	C34	1.363(5)
O12A	N11A	1.25(2)	C34	C35	1.388(4)
N11A	C14A	1.37(2)	C35	C36	1.364(4)
O11A	C11A	1.258(14)	N41	C42	1.344(3)
O13A	C12A	1.207(14)	N41	C46	1.334(3)
O14A	C13A	1.222(15)	C42	C43	1.378(4)
N12A	C11A	1.382(14)	C43	C44	1.368(4)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N12A	C12A	1.387(14)	C44	C45	1.378(5)
N12A	C15A	1.472(15)	C45	C46	1.372(4)
N13A	C12A	1.375(14)			

Table S5 Bond Angles for **2**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O11	Zn1	N11	74.21(10)	C12A	N13A	C16A	116.1(16)
O11	Zn1	N21	90.47(11)	C13A	N13A	C16A	119.2(16)
O12A	Zn1	N21	93.1(4)	O11A	C11A	N12A	117.3(14)
O11A	Zn1	O12A	84.8(6)	O11A	C11A	C14A	125.4(13)
O11A	Zn1	O21	165.0(5)	N12A	C11A	C14A	116.6(13)
O11A	Zn1	N21	92.8(6)	O13A	C12A	N12A	121.6(17)
O11A	Zn1	N31	96.0(6)	O13A	C12A	N13A	119.7(16)
O11A	Zn1	N41	98.4(4)	N13A	C12A	N12A	118.6(13)
O21	Zn1	N11	103.51(9)	O14A	C13A	N13A	119.1(14)
O21	Zn1	O11	166.61(11)	O14A	C13A	C14A	124.8(15)
O21	Zn1	O12A	85.8(4)	N13A	C13A	C14A	115.8(13)
O21	Zn1	N21	76.15(7)	N11A	C14A	C11A	124.8(13)
O21	Zn1	N41	92.00(8)	N11A	C14A	C13A	113.0(14)
N21	Zn1	N11	83.69(10)	C13A	C14A	C11A	122.1(13)
N31	Zn1	N11	94.99(10)	C21	O21	Zn1	114.08(14)
N31	Zn1	O11	99.16(12)	O22	N21	Zn1	124.38(18)
N31	Zn1	O12A	82.2(4)	O22	N21	C24	121.7(2)
N31	Zn1	O21	94.17(8)	C24	N21	Zn1	113.91(16)
N31	Zn1	N21	169.56(8)	C21	N22	C22	124.1(2)
N31	Zn1	N41	92.72(9)	C21	N22	C25	118.8(2)
N41	Zn1	N11	162.09(9)	C22	N22	C25	117.0(2)
N41	Zn1	O11	88.62(9)	C22	N23	C23	124.9(2)
N41	Zn1	O12A	174.2(4)	C22	N23	C26	116.9(2)
N41	Zn1	N21	91.53(9)	C23	N23	C26	118.3(2)
O12	N11	Zn1	125.1(2)	O21	C21	N22	119.6(2)
O12	N11	C14	120.8(3)	O21	C21	C24	123.3(2)
C14	N11	Zn1	113.2(2)	N22	C21	C24	117.1(2)
C11	O11	Zn1	111.6(2)	O23	C22	N22	121.0(3)
C11	N12	C12	123.2(3)	O23	C22	N23	122.0(3)
C11	N12	C15	118.9(3)	N23	C22	N22	117.0(2)
C12	N12	C15	117.7(3)	O24	C23	N23	119.4(3)
C12	N13	C13	125.5(3)	O24	C23	C24	125.5(3)
C12	N13	C16	117.0(3)	N23	C23	C24	115.0(2)
C13	N13	C16	117.3(3)	N21	C24	C21	112.0(2)
O11	C11	N12	118.6(3)	N21	C24	C23	126.3(2)
O11	C11	C14	123.0(3)	C23	C24	C21	121.7(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N12	C11	C14	118.2(3)	C32	N31	Zn1	123.7(2)
O13	C12	N12	121.2(4)	C36	N31	Zn1	119.09(18)
O13	C12	N13	122.2(4)	C36	N31	C32	117.2(3)
N13	C12	N12	116.6(3)	N31	C32	C33	122.5(3)
O14	C13	N13	119.8(3)	C34	C33	C32	119.4(3)
O14	C13	C14	125.6(3)	C33	C34	C35	118.5(3)
N13	C13	C14	114.4(3)	C36	C35	C34	119.0(3)
N11	C14	C11	112.1(3)	N31	C36	C35	123.4(3)
N11	C14	C13	127.0(3)	C42	N41	Zn1	122.01(18)
C13	C14	C11	120.8(3)	C46	N41	Zn1	119.67(19)
N11A	O12A	Zn1	123.5(12)	C46	N41	C42	118.2(2)
O12A	N11A	C14A	123.5(16)	N41	C42	C43	121.9(3)
C11A	O11A	Zn1	125.0(14)	C44	C43	C42	119.0(3)
C11A	N12A	C12A	123.1(13)	C43	C44	C45	119.5(3)
C11A	N12A	C15A	121.4(15)	C46	C45	C44	118.3(3)
C12A	N12A	C15A	115.1(14)	N41	C46	C45	122.9(3)
C12A	N13A	C13A	123.2(13)				

Table S6 Calculated CAS(8,5)/NEVPT2 transition energies and SOC splitting of the ground state for the complex **1**

Root	Multiplicity	ΔE/cm^{-1}	ΔE^{SOC}/cm^{-1}
0	3	0	0, 4.6, 5.2
1	3	11571	
2	3	11941	
3	3	14201	
0	1	15929	
1	1	16455	
4	3	19657	
5	3	21061	
6	3	21805	
2	1	27264	
3	1	27582	
4	1	29814	
5	1	30016	
7	3	30927	
8	3	32330	
9	3	32699	
6	1	34424	
7	1	36198	
8	1	36475	
9	1	44453	
10	1	44920	
11	1	45199	
12	1	45610	
13	1	45612	
14	1	69902	

Table S7 Individual contributions to *D* and *E* of the excited triplet and singlet states computed at the CAS(8,5)/NEVPT2 level for the complex **1**

Root	Multiplicity	D/cm^{-1}	E/cm^{-1}
1.	3	18.23	18.20
2	3	15.55	–16.91
3	3	–27.20	–0.852
4	3	0.060	–0.044
5	3	0.023	0.015
6	3	0.022	0
7	3	0	0
8	3	0	0
9	3	0	0
0	1	0	0
1	1	0	0
2	1	–6.94	–6.85
3	1	–6.71	6.66
4	1	12.20	0
5	1	0	0
6	1	–0.030	0.020
7	1	0	0
8	1	–0.040	0.012
9	1	0	0
10	1	0.028	0
11	1	0.252	0.253
12	1	–0.374	–0.438
13	1	0.289	0.245
14	1	0	0

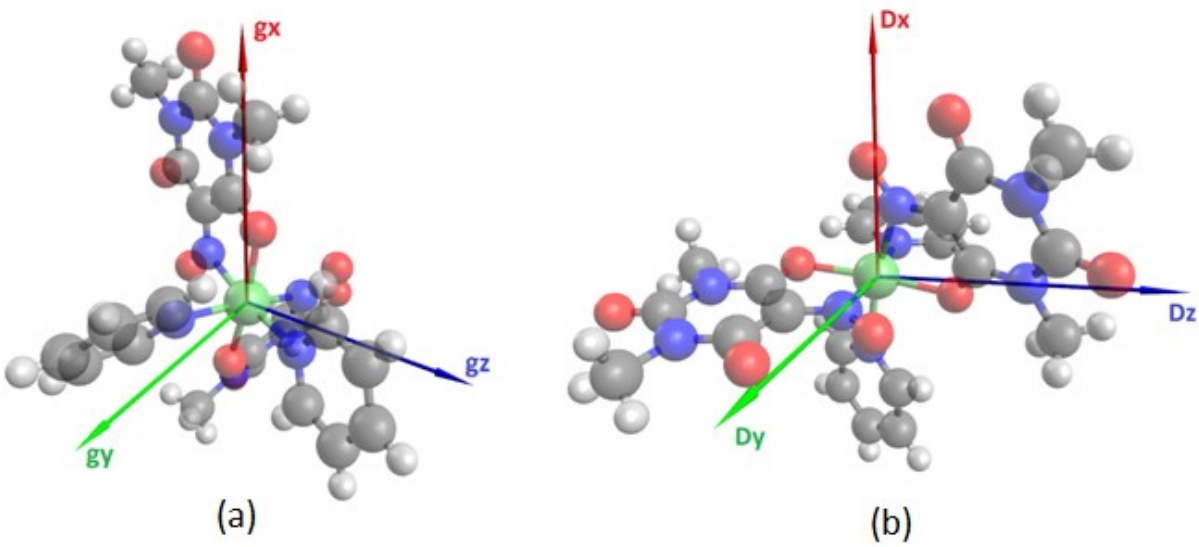

Fig. S3 Visualization of (a) *g*- and (b) *D*-tensor orientation (magnetic axes) in molecular frame of **1**.

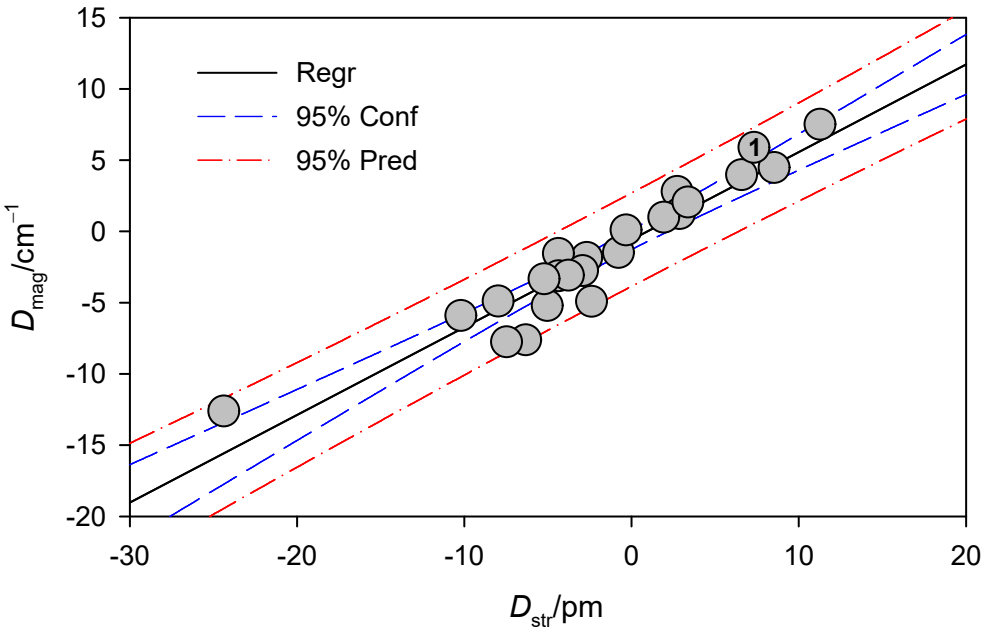

Fig. S4 Magnetostructural *D*-correlation for hexacoordinate Ni(II) complexes with inclusion of the complex **1**. Correlation: $D_{mag}[cm^{-1}] = –0.58 + 0.61D_{str}[pm]$, $R^2 = 0.90$.