Electronic Supporting Information
for

Effective tuning of magnetic anisotropy in distorted pentagonal bipyramidal Ni(II) complexes via substitution of axial co-ligands

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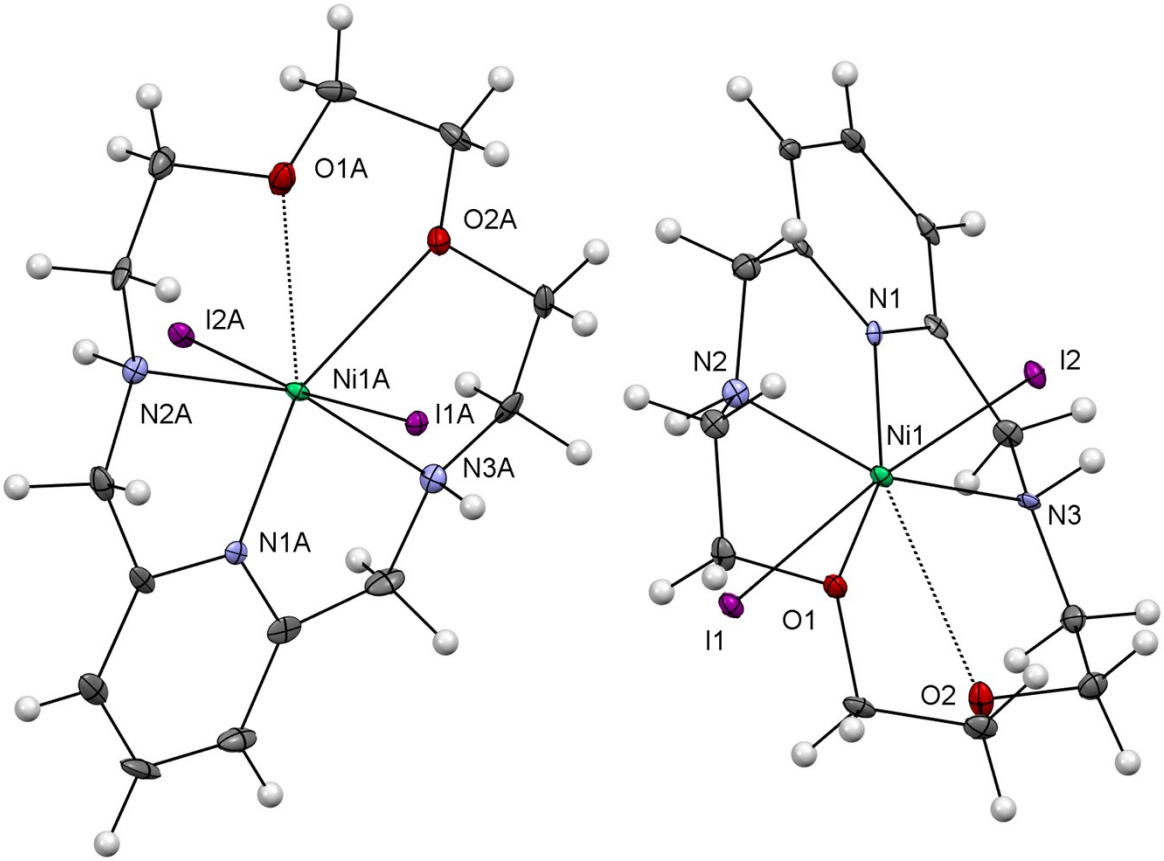


Figure S1: Two crystallographically independent molecules found in the asymmetric unit of the crystal structure of complex **2**. Non-hydrogen atoms are drawn as thermal ellipsoids at the 30% probability level. Hydrogen atoms, except those in macrocyclic NH groups, were omitted for clarity.

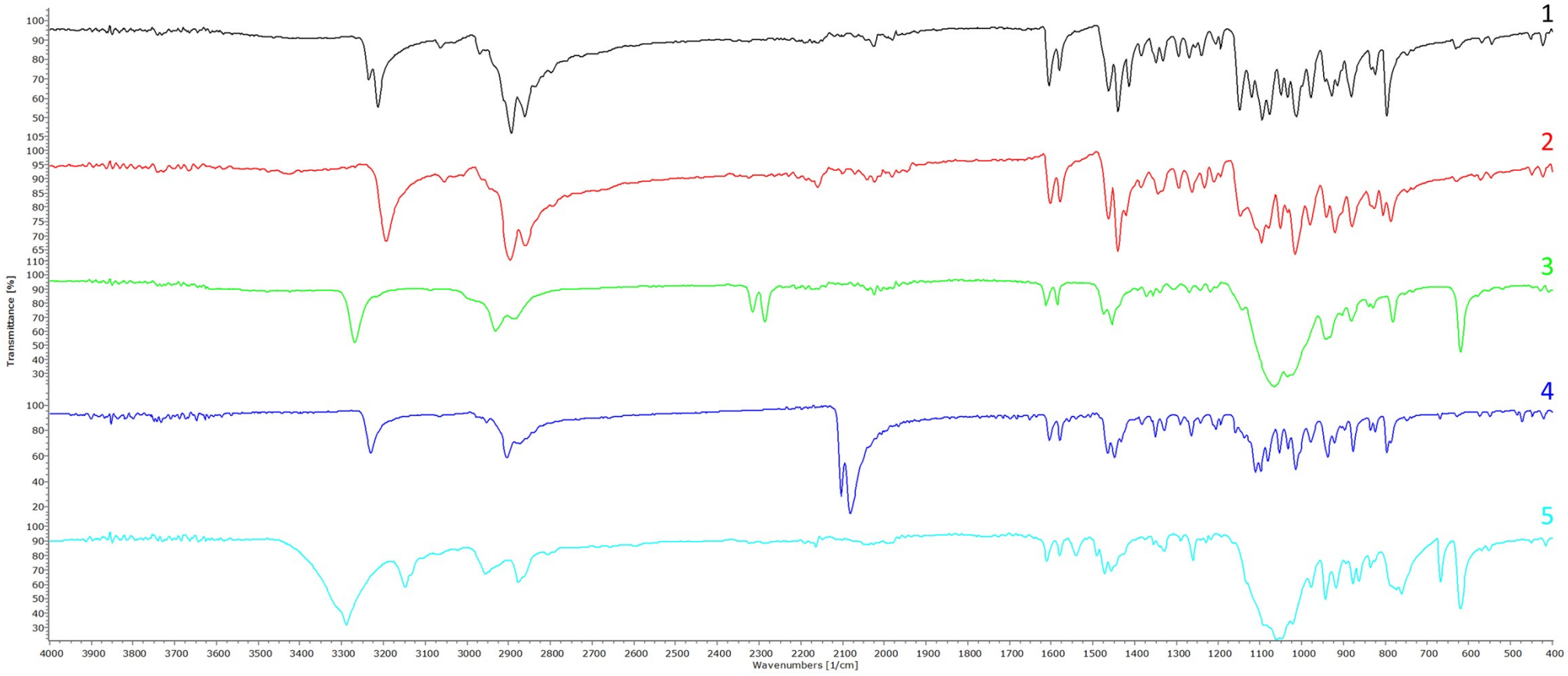
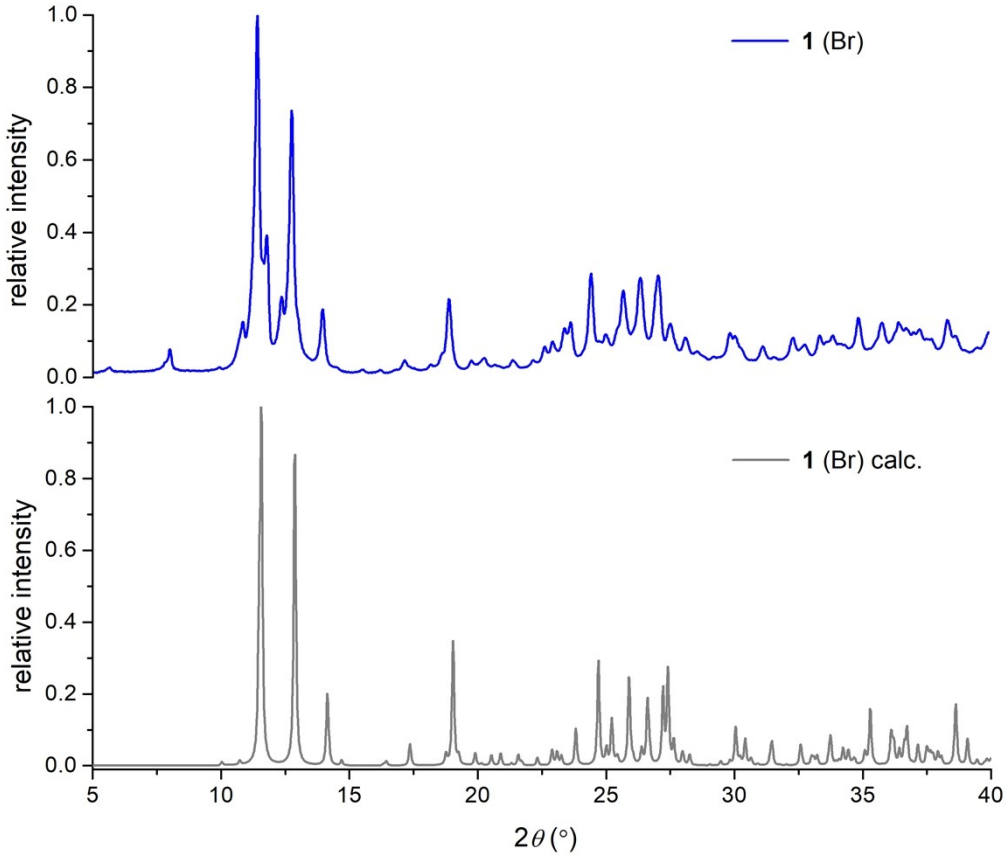
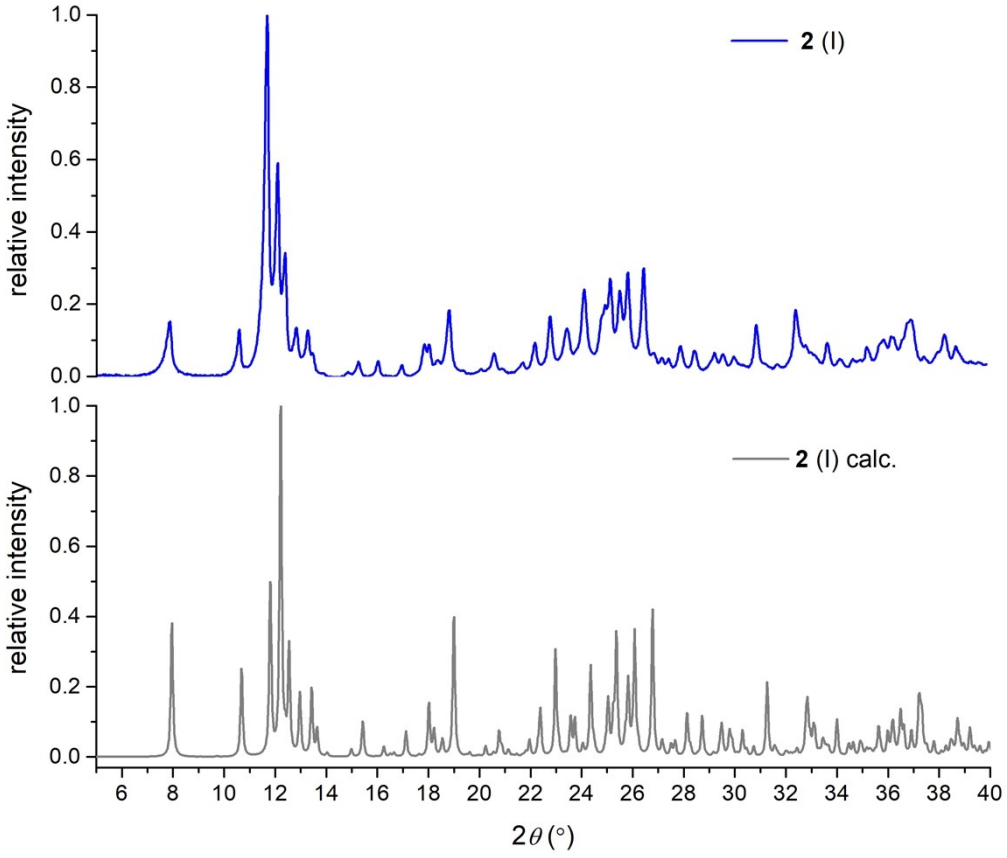
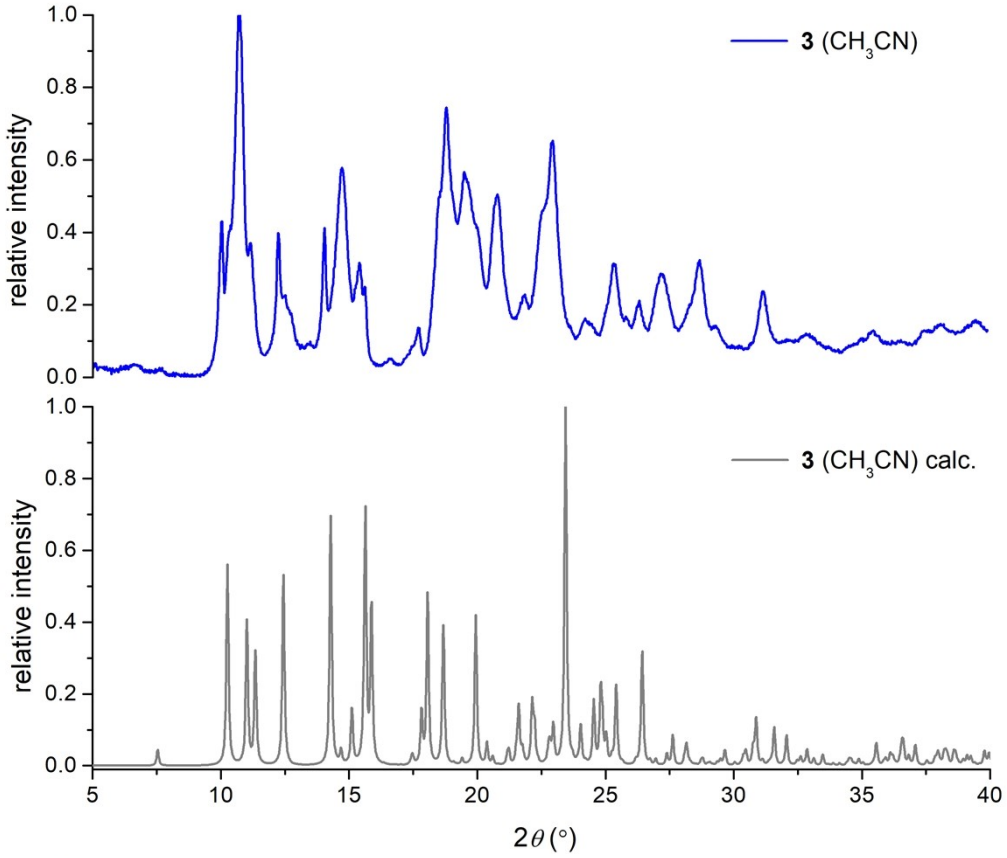
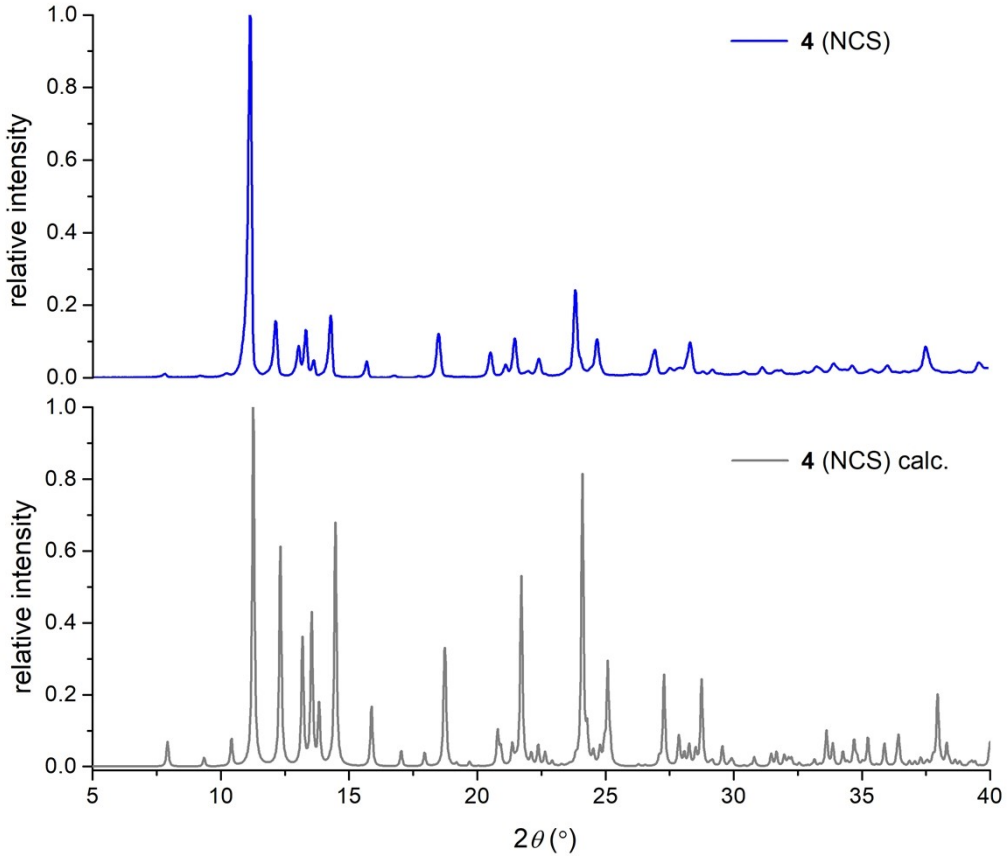


Figure S2: Comparison of IR spectra of the studied Ni(II) complexes **1** (*black*), **2** (*red)*, **3** (*green*), **4** (*blue*) and **5** (*light blue*).


1 (Br)
1 (Br) calc.
relative intensity
2θ (°)


2 (I)
2 (I) calc.
relative intensity
2θ (°)


relative intensity
3 (CH3CN)
3 (CH3CN) calc.
2θ (°)


relative intensity
4 (NCS)
4 (NCS) calc.
2θ (°)

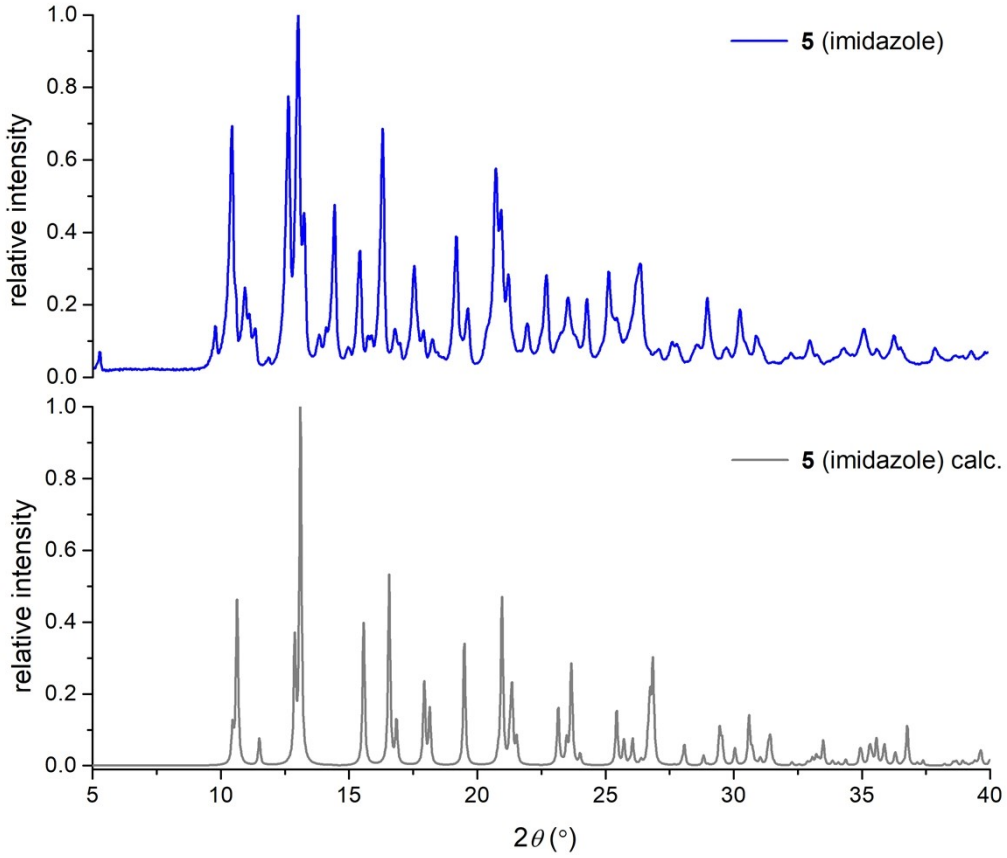


Figure S3: X-ray powder diffraction patterns of studied Ni(II) complexes **1**–**5** together with their comparison with simulated data from single-crystal X-ray analysis.

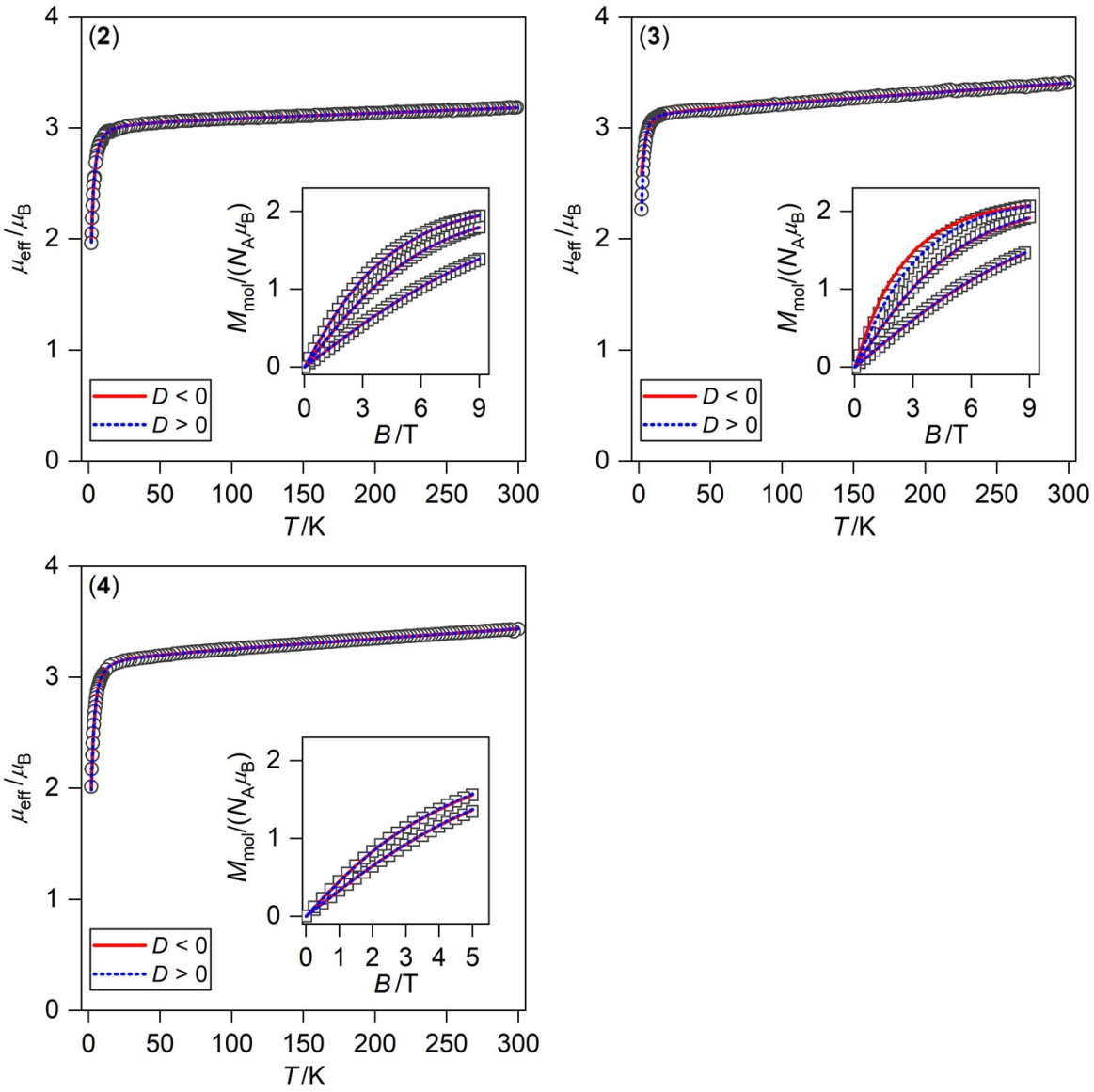


Figure S4: Magnetic data for compounds **2**, **3** and **4**. Temperature dependence of the effective magnetic moment and the isothermal magnetizations measured at $T = 2$, 5, and 10 K in the inset. The empty symbols represent the experimental data points, and the full red lines represent the best fits calculated with negative D-values, and the dotted blue lines were calculated with positive D-values - parameters are listed in manuscript in Table 2.

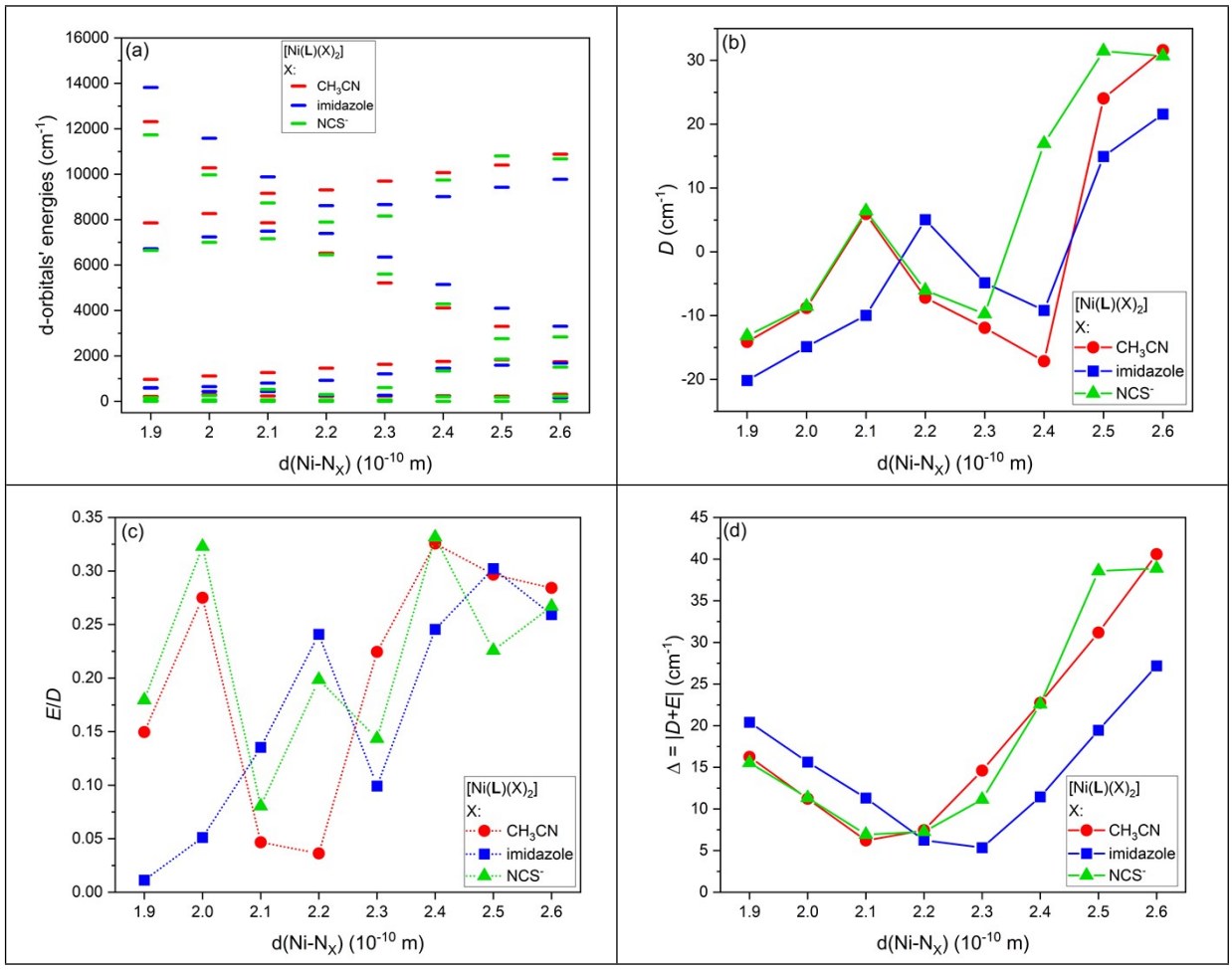


Figure S5: Graphical output of the CASSCF/NEVPT2 calculations for the model compound $[Ni(L)(X)_2]$ complexes (X = NCS^-, CH_3CN and IMID) in which bond length Ni-N_X was varied between 1.9 and 2.6 Å. a) the d-orbitals splitting; b) variation of *D* parameters; c) variation of *E*/*D* parameters; d) variation of |*D*+*E*| parameter.

Table S1 Crystal data and structure refinements for studied complexes

Compound	**3**	**4**
Formula	$C_{17}H_{27}Cl_2N_5NiO_{10}$	$C_{15}H_{21}N_5NiO_2S_2$
M_r	591.04	426.20
Temperature (K)	120(2)	120(2)
Colour	blue	blue
Crystal system	monoclinic	triclinic
Space group	Cc	P–1
a (Å)	19.6899(13)	8.5801(7)
b (Å)	15.9806(10)	9.6096(7)
c (Å)	17.8087(18)	11.3950(8)
α (°)	90	80.387(3)
β (°)	118.943(2)	82.456(3)
γ (°)	90	85.036(3)
V, Å^3	4903.7(7)	916.31(12)
Z	8	2
D_{calc}, g cm^{-3}	–	1.545
μ, mm^{-1}	–	1.306
F(000)	–	444
θ range for data collection (°)	–	2.4– 27.5
Refl. collected	–	18985
Independent refl.	–	4193
R(int)	–	0.0419
Data/restrains/parameters	–	4193/0/ 234
Completeness to θ (%)	–	99.5
Goodness-of-fit on F^2	–	1.116
$R1$, w$R2$ ($I>2\sigma(I)$[a]	–	0.0327, 0.0778
$R1$, w$R2$ (all data)[a]	–	0.0446, 0.0882
Largest diff. peak and hole / A^{-3}	–	0.521 and –0.663
CCDC number	–	2203812

[a] $R_1 = \Sigma(\left|F_o\right| - \left|F_c\right|) / \Sigma\left|F_c\right|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Table S2: Results of continuous shape measures calculations using program Shape 2.1 for compounds **1–5**.[a]

	Cl[e]	**1**-Br	**2**-I		**3**-CH_3CN	**4**-NCS	**5**-imid
CN=7[b] $\{NiN_3O_2X_2\}$							
HP-7	34.400	33.911	35.074	35.269	31.498	32.067	33.493
HPY-7	24.354	23.556	24.435	24.264	23.098	23.444	24.795
PBPY-7	1.000	1.737	1.896	1.792	1.457	1.294	0.518
COC-7	5.485	5.893	6.423	6.609	5.262	5.183	6.780
CTPR-7	3.893	4.595	5.221	5.080	3.410	3.688	4.842
JPBPY-7	5.456	7.191	8.916	8.971	3.610	3.106	2.711
JETPY-7	21.834	19.879	21.677	23.249	21.059	21.505	23.272
CN=6[c] $\{NiN_3OX_2\}$							
HP-6	27.770	29.344	28.596	28.992	27.408	27.309	28.874
PPY-6	21.128	22.545	22.730	22.614	20.242	18.603	18.886
OC-6	4.438	4.148	5.177	5.624	4.408	5.030	5.427
TPR-6	9.340	9.752	10.879	10.741	9.917	8.855	9.195
JPPY-6	23.492	24.323	24.233	23.991	23.147	21.905	22.327
CN=5[d] $\{NiN_3O_2\}$							
PP-5	1.212	1.902	1.459	1.125	1.331	1.178	0.432
vOC-5	25.753	25.785	25.900	26.458	25.221	25.162	28.784
TBPY-5	30.325	30.991	30.645	31.039	30.115	29.977	33.416
SPY-5	26.638	27.067	27.045	27.269	26.256	26.013	29.636
JTBPY-5	31.141	30.307	31.041	31.524	30.543	30.219	34.132
CN=5[d] $\{NiN_3X_2\}$							
PP-5	31.274	30.525	32.302	31.532	32.322	31.820	33.093
vOC-5	1.912	2.705	3.750	3.845	1.137	1.621	2.151
TBPY-5	6.763	8.296	9.466	10.139	5.673	5.204	5.071
SPY-5	4.999	6.140	7.198	7.433	4.104	4.680	5.379
JTBPY-5	9.444	11.620	11.581	11.174	6.594	6.032	6.036

[a] The listed valued correspond to the deviation between the ideal and real coordination polyhedra, the lowest values are in red color.
[b] HP-7 = heptagon, HPY-7 = hexagonal pyramid, PBPY-7= pentagonal bipyramid, COC-7 = capped octahedron, CTPR-7 = capped trigonal prism, JPBPY-7 = Johnson pentagonal bipyramid J13, JETPY-7 = Johnson elongated triangular pyramid J7.
[c] HP-6 = hexagon, PPY-6 pentagonal pyramid, OC-6 = octahedron, TPR-6 = trigonal prism, JPPY-6 = Johnson pentagonal pyramid J2.
[d] PP-5 = Pentagon, vOC-5 = Vacant octahedron, TBPY-5 = Trigonal bipyramid, SPY-5 = Spherical square pyramid, JTBPY-5 = Johnson trigonal bipyramid.
[e] ref. B. Drahoš, R. Herchel and Z. Trávníček, *Inorg. Chem.*, **2015**, *54*, 3352–3369.

Table S3: Calculated QTAIM parameters (electron density $\rho(\mathbf{r})$, the potential energy density $V(\mathbf{r})$, the energy density $h_e(\mathbf{r})$ and the Laplacian of $\rho(\mathbf{r})$ ($\nabla^2\rho(\mathbf{r})$) at BCP belonging to donor-acceptor bonds.

[Ni**L**Br_2] (**1**)						
Bond	Length	$\rho(\mathbf{r})$	$V(\mathbf{r})$	$h_e(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{int}
Ni-N(py)	1.987	9.01E-02	-1.57E-01	-3.04E-02	3.86E-01	49.35
Ni-N1(aliph)	2.104	7.10E-02	-1.09E-01	-2.09E-02	2.68E-01	34.14
Ni-N2(aliph)	2.159	6.27E-02	-8.93E-02	-1.63E-02	2.27E-01	28.03
Ni-O1	2.319	3.50E-02	-4.24E-02	-7.91E-04	1.63E-01	13.29
Ni-O2	2.966	1.12E-02	-7.57E-03	3.23E-04	3.29E-02	2.37
Ni-X1	2.537	4.84E-02	-5.13E-02	-1.04E-02	1.22E-01	16.08
Ni-X2	2.590	4.36E-02	-4.43E-02	-8.33E-03	1.11E-01	13.90
[Ni**L**I_2] (**2**) (Ni1)						
Bond	Length	$\rho(\mathbf{r})$	$V(\mathbf{r})$	$h_e(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{int}
Ni-N(py)	1.996	8.84E-02	-1.53E-01	-2.95E-02	3.76E-01	47.99
Ni-N1(aliph)	2.110	7.03E-02	-1.06E-01	-2.05E-02	2.62E-01	33.41
Ni-N2(aliph)	2.167	6.18E-02	-8.70E-02	-1.57E-02	2.22E-01	27.31
Ni-O1	2.349	3.29E-02	-3.83E-02	-1.89E-04	1.52E-01	12.01
Ni-O2	2.823	1.41E-02	-1.03E-02	4.61E-04	4.51E-02	3.25
Ni-X1	2.797	3.89E-02	-3.23E-02	-7.02E-03	7.29E-02	10.12
Ni-X2	2.779	4.00E-02	-3.40E-02	-7.45E-03	7.64E-02	10.67
[Ni**L**I_2] (**2**) (Ni2)						
Bond	Length	$\rho(\mathbf{r})$	$V(\mathbf{r})$	$h_e(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{int}
Ni-N(py)	1.991	8.95E-02	-1.55E-01	-3.01E-02	3.81E-01	48.78
Ni-N1(aliph)	2.127	6.78E-02	-1.00E-01	-1.91E-02	2.48E-01	31.39
Ni-N2(aliph)	2.114	6.97E-02	-1.05E-01	-2.02E-02	2.58E-01	32.89
Ni-O1	2.676	1.78E-02	-1.45E-02	8.38E-04	6.49E-02	4.56
Ni-O2	2.500	2.44E-02	-2.36E-02	9.90E-04	1.02E-01	7.41
Ni-X1	2.784	3.98E-02	-3.34E-02	-7.35E-03	7.49E-02	10.49
Ni-X2	2.821	3.71E-02	-3.04E-02	-6.33E-03	7.09E-02	9.53
[Ni**L**$(CH_3CN)_2$]$(ClO_4)_2$ (**3**)						
Bond	Length	$\rho(\mathbf{r})$	$V(\mathbf{r})$	$h_e(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{int}
Ni-N(py)	1.930	1.05E-01	-1.90E-01	-3.93E-02	4.44E-01	59.48
Ni-N1(aliph)	2.111	7.13E-02	-1.07E-01	-2.11E-02	2.59E-01	33.58
Ni-N2(aliph)	2.119	6.98E-02	-1.04E-01	-2.02E-02	2.54E-01	32.63
Ni-O1	2.459	2.65E-02	-2.69E-02	8.65E-04	1.15E-01	8.46
Ni-O2	2.693	1.76E-02	-1.41E-02	6.92E-04	6.21E-02	4.43
Ni-X1	2.054	7.00E-02	-1.23E-01	-1.83E-02	3.44E-01	38.50
Ni-X2	2.062	6.86E-02	-1.20E-01	-1.77E-02	3.36E-01	37.51

[Ni**L**$(NCS)_2$] (**4**)						
Bond	Length	$\rho(\mathbf{r})$	$V(\mathbf{r})$	$h_e(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	E_{int}
Ni-N(py)	2.000	8.72E-02	-1.51E-01	-2.87E-02	3.74E-01	47.36
Ni-N1(aliph)	2.150	6.39E-02	-9.31E-02	-1.69E-02	2.38E-01	29.23
Ni-N2(aliph)	2.157	6.30E-02	-9.06E-02	-1.64E-02	2.31E-01	28.41
Ni-O1	2.447	2.69E-02	-2.78E-02	9.69E-04	1.19E-01	8.72
Ni-O2	2.639	1.88E-02	-1.58E-02	1.04E-03	7.17E-02	4.97
Ni-X1	2.037	7.46E-02	-1.26E-01	-2.15E-02	3.34E-01	39.64
Ni-X2	2.029	7.62E-02	-1.32E-01	-2.17E-02	3.54E-01	41.39
[NiL$(imidazole)_2$]$(ClO_4)_2$ (**5**)						
Bond	Length	r(r)	V(r)	he(r)	∇2ρ(r)	Eint
Ni-N(py)	2.008	8.69E-02	-1.48E-01	-2.88E-02	3.62E-01	46.43
Ni-N1(aliph)	2.194	5.90E-02	-8.09E-02	-1.41E-02	2.11E-01	25.39
Ni-N2(aliph)	2.194	5.90E-02	-8.09E-02	-1.41E-02	2.11E-01	25.39
Ni-O1	2.473	2.66E-02	-2.65E-02	7.83E-04	1.12E-01	8.31
Ni-O2	2.473	2.66E-02	-2.65E-02	7.83E-04	1.12E-01	8.31
Ni-X1	2.079	7.17E-02	-1.16E-01	-2.04E-02	3.00E-01	36.29
Ni-X2	2.079	7.17E-02	-1.16E-01	-2.04E-02	3.00E-01	36.29
[NiLCl2]						
Bond	Length	r(r)	V(r)	he(r)	∇2ρ(r)	Eint
Ni-N(py)	1.987	8.98E-02	-1.58E-01	-3.00E-02	3.91E-01	49.53
Ni-N1(aliph)	2.132	6.59E-02	-9.81E-02	-1.80E-02	2.48E-01	30.78
Ni-N2(aliph)	2.118	6.80E-02	-1.03E-01	-1.91E-02	2.59E-01	32.36
Ni-O1	2.506	2.35E-02	-2.27E-02	1.23E-03	1.01E-01	7.14
Ni-O2	2.663	1.78E-02	-1.47E-02	1.00E-03	6.70E-02	4.63
Ni-X1	2.381	5.58E-02	-7.03E-02	-1.40E-02	1.69E-01	22.06
Ni-X2	2.391	5.45E-02	-6.84E-02	-1.34E-02	1.67E-01	21.45

Table S4: Calculated individual non-zero contributions to *D*-tensor for [Ni**L**Br_2] (**1**), [Ni**L**I_2] (**2**), [Ni**L**$(CH_3CN)_2$]$(ClO_4)_2$ (**3**), [Ni**L**$(NCS)_2$] (**4**), [NiL(imidazole)$_2$]$(ClO_4)_2$ (**5**) and [Ni**L**Cl_2] obtained from the calculation based on CASSCF/NEVPT2 using the effective Hamiltonian theory.

[Ni**L**Br_2] (**1**)				[Ni**L**I_2] (**2**) – Ni1				[Ni**L**I_2] (**2**) – Ni2			
Mult	Root	D	E	Mult	Root	D	E	Mult	Root	D	E
3	0	-0.000	0.000	3	0	0.000	-0.000	3	0	0.000	-0.000
3	1	23.181	23.319	3	1	25.407	22.584	3	1	26.132	26.529
3	2	1.658	-11.659	3	2	21.280	-17.591	3	2	17.014	-19.560
3	3	-21.269	-7.283	3	3	-44.372	0.033	3	3	-39.803	-1.219
3	4	-0.158	0.054	3	4	-0.174	0.061	3	4	-0.706	0.043
3	5	0.163	-0.107	3	5	0.361	-0.098	3	5	0.644	-0.623
3	6	-0.111	-0.030	3	6	0.215	-0.199	3	6	0.032	0.077
3	7	0.004	-0.003	3	7	-0.005	-0.000	3	7	-0.009	-0.001
3	8	-0.013	-0.013	3	8	0.054	-0.055	3	8	0.050	-0.061
3	9	0.013	0.010	3	9	0.031	0.030	3	9	0.027	0.030
1	0	-0.003	-0.002	1	0	0.006	-0.001	1	0	-0.002	-0.002
1	1	-0.001	0.001	1	1	0.001	0.000	1	1	-0.001	0.000
1	2	-7.290	-7.409	1	2	-7.093	-7.083	1	2	-7.158	-7.302
1	3	1.625	3.911	1	3	-6.415	6.368	1	3	-4.941	5.993
1	4	5.166	3.003	1	4	14.133	0.009	1	4	12.277	0.512
1	5	-0.002	0.002	1	5	0.109	-0.005	1	5	0.284	-0.001
1	6	0.041	0.000	1	6	0.001	0.001	1	6	-0.001	0.001
1	7	0.059	0.030	1	7	-0.067	0.066	1	7	-0.045	0.072
1	8	0.008	0.011	1	8	-0.064	0.052	1	8	-0.007	-0.003
1	9	0.017	0.022	1	9	0.062	0.001	1	9	-0.010	0.009
1	10	0.028	0.067	1	10	-0.846	0.475	1	10	-0.643	-0.678
1	11	0.006	-0.081	1	11	-0.113	-0.111	1	11	-0.600	0.283
1	12	-0.929	0.034	1	12	-0.912	-0.182	1	12	-0.572	0.609
1	13	1.133	0.094	1	13	2.021	-0.044	1	13	1.988	-0.013
1	14	0.000	0.000	1	14	0.001	0.000	1	14	0.000	-0.000

[Ni**L**$(CH_3CN)_2$]$(ClO_4)_2$ (**3**),				[Ni**L**$(NCS)_2$] (**4**)				[NiL(imidazole)$_2$]$(ClO_4)_2$ (**5**)			
Mult	Root	D	E	Mult	Root	D	E	Mult	Root	D	E
3	0	0.000	0.000	3	0	0.000	-0.000	3	0	-0.000	-0.000
3	1	19.715	-19.034	3	1	25.383	-25.152	3	1	27.012	27.012
3	2	17.919	17.592	3	2	21.091	21.737	3	2	-41.613	0.000
3	3	-33.485	0.471	3	3	-37.335	0.518	3	3	19.314	-19.314
3	4	-0.087	-0.000	3	4	-0.149	0.089	3	4	0.110	-0.110
3	5	0.043	-0.009	3	5	0.032	0.132	3	5	-0.462	0.000
3	6	0.017	-0.018	3	6	0.124	0.049	3	6	0.021	0.021
3	7	0.003	-0.001	3	7	-0.013	0.000	3	7	0.004	-0.004
3	8	-0.004	-0.000	3	8	0.019	0.019	3	8	-0.029	0.000
3	9	0.000	-0.001	3	9	0.004	-0.003	3	9	0.002	0.002
1	0	0.000	-0.000	1	0	-0.004	0.004	1	0	-0.000	0.000
1	1	-0.000	-0.000	1	1	-0.000	-0.000	1	1	-0.000	0.000
1	2	-7.164	2.857	1	2	-7.939	7.935	1	2	-8.219	-8.219
1	3	-7.074	-2.650	1	3	-7.221	-7.300	1	3	14.045	-0.000
1	4	13.405	-0.058	1	4	13.657	-0.034	1	4	-6.843	6.843
1	5	0.001	-0.000	1	5	0.003	-0.000	1	5	-0.000	0.000
1	6	-0.046	0.009	1	6	0.121	-0.008	1	6	-0.034	0.034
1	7	0.056	0.000	1	7	-0.112	-0.107	1	7	0.085	-0.000
1	8	0.000	0.001	1	8	-0.014	0.004	1	8	0.001	-0.010
1	9	0.008	-0.000	1	9	-0.004	-0.016	1	9	-0.000	0.000
1	10	0.763	-0.030	1	10	-0.203	0.204	1	10	-0.004	0.004
1	11	-0.340	-0.201	1	11	-0.214	0.330	1	11	2.038	-0.002
1	12	0.454	-0.105	1	12	-0.180	-0.308	1	12	-1.026	1.026
1	13	-0.635	0.299	1	13	0.890	-0.316	1	13	-0.679	-0.683
1	14	-0.000	0.000	1	14	-0.000	0.000	1	14	-0.000	0.000

[Ni**L**Cl_2]			
Mult	Root	D	E
3	0	0.000	-0.000
3	1	26.139	26.043
3	2	-45.410	-0.016
3	3	21.079	-20.949
3	4	-0.108	-0.053
3	5	-0.024	-0.070
3	6	-0.053	0.004
3	7	0.007	-0.007
3	8	-0.014	0.000
3	9	-0.001	-0.000
1	0	-0.001	-0.000
1	1	0.000	0.000
1	2	-7.736	-7.787
1	3	13.356	0.314
1	4	-5.973	6.705
1	5	-0.001	0.001
1	6	-0.027	0.033
1	7	0.066	-0.002
1	8	0.000	0.001
1	9	-0.025	0.023
1	10	0.039	0.001
1	11	0.113	-0.537
1	12	0.751	0.076
1	13	-0.610	0.609
1	14	0.000	-0.000