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Electronic Supporting Information

Deciphering the influence of structural distortions on single ion magnetic anisotropy of pentagonal bipyramidal Ni(II) complexes

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Materials and Methods

Starting materials were procured from commercial sources and used as received. Solvents were purified by conventional techniques and distilled prior to use. Elemental analyses were performed on a Perkin Elmer Model PR 2400 Series II Elemental Analyzer. Infrared spectra were recorded on a Nicolet Impact I-410 FT-IR spectrometer as KBr diluted discs and a Perkin Elmer MIR-FIR FT-IR spectrometer. Thermogravimetric analyses were performed on a Shimadzu TGA-50 thermal analyzer. The UVvisible spectra were recorded in a Shimadzu UV 2550 spectrophotometer. Melting points were recorded on a Buchi M-560 Melting Point apparatus and are reported uncorrected. Magnetic susceptibility data were collected on microcrystalline samples over 300-2 K temperature range with an applied field of 1000 Oe using a MPMS SQUID magnetometer. Magnetization studies were performed between 0-5/7 T at 2-3.6 K, 5 K, 7 K and 10 K. Fitting of magnetization data was performed by PHI 3.1.5 software using a two-step procedure. Initially, $\chi_M T$ vs T plots were fitted to evaluate the isotropic g parameters. During the fitting of $\chi_M T$ vs T plots, D parameter was also introduced to fit low temperature regime. Thereafter, simultaneous fitting of $\chi_M T$ vs T plots and M vs H plots were carried out by using PHI programme to estimate the D and E parameters reliably. The isotropic g values obtained from fitting of $\chi_M T$ vs T plots were kept fixed during the simultaneous fitting of $\chi_M T$ vs T plots and M vs H plots.

2,6-diacetylpyridine bis(semicarbazone) i.e., L1, 2, 6-diacetylpyridine bis(benzoyl hydrazone) i.e., L2, $[Ni(L1)(H_2O)_2](NO_3)_2$ and $[Ni(L2)(H_2O)_2](NO_3)_2$ were prepared according to the reported literature procedure.¹⁻²

Single Crystal X-Ray Diffraction Studies

Suitable single crystals of all the compounds were obtained directly from the reaction mixtures were used for diffraction measurements. The diffraction data for the compounds were collected on a Bruker APEX-II CCD diffractometer using MoK α radiation (λ =0.71073 Å) using φ and ω scans of narrow (0.5°) frames at 90-100K. All the structures were solved by direct methods using SHELXL-97 as implemented in the WinGX program system.³ Anisotropic refinement was executed on all non-hydrogen atoms. The aliphatic and aromatic hydrogen atoms were placed on calculated positions but were allowed to ride on their parent atoms during subsequent cycles of refinements. Positions of N-H and O-H hydrogen atoms were located on a difference Fourier map and allowed

to ride on their parent atoms during subsequent cycles of refinements. Disordered lattice water molecules and two nitrate counter anions present in structure of 1 are removed using PLATON SQUEEZE program.⁴ The geometry around the Ni(II) center of mononuclear compounds **1-3** was examined using continuous shape measures analysis carried out with SHAPE program.⁵ The data obtained from the analysis for compounds **1-3** are listed in Table S4-S5. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC 1936566 (**1**), CCDC 1936571 (**2**) and CCDC 1425683 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Computational details

All calculations were performed with the ORCA 4.1.0 package using the experimental geometries without any further structure optimization.⁶ Resolution of identity (RI) approximation with the decontracted auxiliary def2-TZVP or def2-TZVP/C Coulomb fitting basis set along with tight SCF convergence criteria were employed in all calculations. The d⁸ configuration of Ni^{II} gives rise to ten S = 1 and fifteen S = 0electronic multiplets. We computed nonrelativistic energy levels and wave functions using the complete active space self-consistent field (CASSCF) method, averaging over the electron densities of all considered states and taking an active space with eight electrons distributed over the five 3d orbitals CAS(8,5).⁷ In order to incorporate dynamic correlation, N-electron valence perturbation theory to second order (NEVPT2) calculations were performed on configurational interaction matrices obtained from CASSCF calculations.⁸ The zero field splitting parameters (D & E) were extracted from effective Hamiltonian approach where all matrix elements of the anisotropic spin Hamiltonian are calculated from the ab initio energies and wave functions.⁹ In order to rationalize the magnitude and sign of zero field splitting parameters, the perturbative method implemented in the ORCA code are also performed and the D values extracted by this method are found to be slightly overestimated as compared to those obtained from effective Hamiltonian method. One electron eigen values of the five d-orbitals in compound **1-3** were obtained from ab-initio Ligand Field calculations.¹⁰

Synthesis of [Ni(L1)(imz)2](NO3)2.2H2O (1)

To a solution of $[Ni(L1)(H_2O)_2](NO_3)_2$ (0.1 mmol, 0.0513 g) in methanol (20 mL), a solution of imidazole (0.35 mmol, 0.0238 g) in methanol (10 mL) was added. The reaction mixture was refluxed with stirring for 2 hours. The reaction mixture was cooled to room temperature, filtered and the filtrate was kept undisturbed for slow evaporation. Green block shaped crystals were observed after 10 days. The mother liquor was decanted and crystals were washed with minimum amount of ethanol and then dried with diethyl ether. Yield: 0.046 g (73 % based on Ni); M. p. >250 °C; Elemental analysis: Found C, 32.71%; H, 4.12%; N, 28.61%. C₁₇H₂₇N₁₃O₁₀Ni requires C, 32.28%; H, 4.31%; N, 28.81%. IR (KBr, cm⁻¹): 3191(br), 1675(s), 1621(m), 1537(s), 1384(s), 1352(w), 1196(s),1070(s), 943(w), 826(w), 801(m), 758(m), 662(m), 517(m).

Synthesis of [Ni(L1)(SCN)₂].2H₂O (2)

To a solution of $[Ni(L1)(H_2O)_2](NO_3)_2$ (0.2 mmol, 0.1026 g) in methanol (20mL), an aqueous solution of KSCN (0.42 mmol, 0.0407 g) (5 mL) was added. The reaction mixture was stirred for 2 hours. The reaction mixture was then filtered and the filtrate was kept undisturbed for slow evaporation. Green block shaped crystals were observed after 10 days. The mother liquor was decanted and crystals were washed with minimum amount of ethanol and then dried with diethyl ether. Yield: 0.068 g (70 % based on Ni); M. p. >250 °C; Elemental analysis: Found C, 31.92%; H, 3.99%; N, 25.87%. C₁₃H₁₉N₉O₄S₂Ni requires C, 31.98%; H, 3.93%; N, 25.84%. IR (KBr, cm⁻¹): 3396(br), 2102(s), 2074(s), 1681(s), 1531(m), 1445(w), 1384(m), 1278(m), 1210(m),1094(s), 805(m), 756(m), 520(m), 462(w).

Synthesis of [Ni(L2)(SCN)₂].3H₂O (3)

To a solution of $[Ni(L2)(H_2O)_2](NO_3)_2$ (0.027 mmol, 0.0176 g) in methanol (20 mL), a solution of KSCN (0.056 mmol, 0.0056 g) in H₂O (10 mL) was added. The reaction mixture was stirred at room temperature for 3 hours. The reaction mixture was filtered and the filtrate was kept undisturbed for slow evaporation at room temperature. Green block shaped crystals were observed after a week. The mother liquor was decanted and crystals were washed with minimum amount of ethanol and then dried with diethyl ether. Yield: 0.010 g (59 % based on Ni); M. p. >250 °C; Elemental analysis: Found C, 47.91%; H, 4.21%; N, 15.23%. C₂₅H₂₇N₇O₅S₂Ni requires C, 47.78%; H, 4.33%; N, 15.61%. IR (KBr, cm⁻¹): 3470(br), 2107(w), 2069(s), 1637(s), 1516(m), 1444(m), 1381(w), 1269(s), 1184(s), 1129(w), 1012(m), 897(w), 801(m), 711(m), 554(m), 464(w).

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Figure S1: FT-IR spectra of compound 1-3 as KBr disc



Figure S2: UV-visible spectra of compound **1-3** in DMSO medium



Figure S3: TGA pattern of compound 1-3



Figure S4: Powder X-ray diffraction pattern of as synthesized compound **1** and simulated diffraction pattern generated from single crystal x-ray diffraction data.



Figure S5: Powder X-ray diffraction pattern of as synthesized compound **2** and simulated diffraction pattern generated from single crystal x-ray diffraction data.



Figure S6: Powder X-ray diffraction pattern of as synthesized compound **3** and simulated diffraction pattern generated from single crystal x-ray diffraction data.



Figure S7: Hydrogen bonding network present in compound ${\bf 2}$



Figure S8: Hydrogen bonding network present in compound 3



Figure S9: M vs HT⁻¹ plot of **1** at different temperatures. Circles represent experimental data while solid lines are best fits obtained by PHI.



Figure S10: M vs HT⁻¹ plot of **2** at different temperatures. Circles represent experimental data while solid lines are best fits obtained by PHI.



Figure S11: M vs HT^{-1} plot of **3** at different temperatures. Circles represent experimental data while solid lines are best fits obtained by PHI.



Figure S12: Electronic arrangement in the ground triplet and 1st, 2nd and 3rd excited triplet states



Figure S13: One electron eigen values of d-orbitals in **1-3** obtained from AI-LFT calculations

Complex	1	2	3
Empirical formula	$C_{17}H_{23}N_{11}O_2Ni$	$C_{13}H_{15}N_9O_4S_2Ni$	$C_{25}H_{19}N_7O_5S_2Ni$
Formula weight	472.17	484.15	620.28
Temperature/K	293	293	100
Crystal system	Tetragonal	Triclinic	Orthorhombic
Space group	$I4_1/a$	P-1	$P2_12_12_1$
a/Å	32.159 (12)	8.758 (4)	10.330 (52)
b/Å	32.159 (12)	11.248 (5)	11.455 (3)
c/Å	10.031 (4)	12.524 (6)	23.668 (6)
α/°	90	65.78 (6)	90
β/°	90	84.96 (7)	90
γ/°	90	71.81 (6)	90
Volume/Å ³	10374.6 (9)	1067.8 (9)	2801.06 (12)
Ζ	16	2	4
$\rho_{\text{calc}}, \text{ mg m}^{-3}$	1.209	1.506	1.471
μ/mm ⁻¹	0.780	1.142	0.890
Crystal size, mm ³	0.30x0.24x0.20	0.24x0.23x0.21	0.32x0.27x0.22
Theta range for data collection	1.266 to 28.411°	2.450 to 28.776°	1.721 to 27.710°
F(000)	3936	496	1272
Reflections collected	37717	10441	13706
Independent reflections	6507	5086	6128
Completeness to theta	99.9%	96.3%	99.3%
Data/parameters/restraints	6507/6/314	5086/286/0	6128/363/0
Goodness-of-fit on F ²	1.026	1.032	1.057
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0641, wR_2 = 0.1894$	$R_1 = 0.0588, wR_2 = 0.1625$	$R_1 = 0.0489, wR_2 = 0.1201$
Final R indexes [all data]	$R_1 = 0.1076 \text{ w} R_2 = 0.2088$	$R_1 = 0.0861, wR_2 = 0.1808$	$R_1 = 0.0604, wR_2 = 0.1364$
Largest diff. peak and hole	0.296 and -0.366 e.Å ⁻³	0.604 and -0.541 e.Å ⁻³	0.296 and -0.366 e.Å ⁻³

Table S1. Crystal data and refinement parameters of compounds 1-3

Bonds lengths	1	2	3
Ni(1)-N(1)	2.076(3)	2.021 (8)	2.013(4)
Ni(1)-N(2)	2.142(2)	2.192 (7)	2.081(5)
Ni(1)-N(4)	2.228(3)	2.122 (9)	2.158(5)
Ni(1)-O(1)	2.290(2)	2.692 (8)	2.314(4)
Ni(1)-O(2)	2.495	2.393 (1)	2.685
Ni(1)-Naxial-1	2.066(3)	1.999 (9)	2.027(5)
Ni(1)-Naxial-2	2.051(3)	2.003 (7)	2.006(5)
Bond Angles			
O(1)-Ni(1)-N(2)	71.24 (1)	65.15 (1)	72.38(2)
N(2)-Ni(1)-N(1)	74.28 (1)	74.67 (1)	76.30(2)
N(1)-Ni(1)-N(4)	73.13 (1)	75.46 (2)	75.38(2)
N(4)-Ni(1)-O(2)	66.99	70.49 (2)	65.07
O(2)-Ni(1)-O(1)	74.37	74.16 (1)	71.16
N(1)-Ni(1)-Naxial-1	94.34 (1)	95.52 (1)	93.72(2)
N(1)-Ni(1)-Naxial-2	93.59 (1)	99.02 (2)	93.02(2)

Table S2: Selected bond lengths (Å) and bond angles (°) of compounds 1-3

Table S3. Hydrogen bonding parameters of compounds 2-3

Complex	Interactions	HA (Å)	D A(Å)	∠ D – H A (°)	Symmetry
	N(3)-H(3D) S(1)	2.60	3.421(16)	159.0	2-x,-y,1-z
	N(5)-H(5D) ···O(102)	2.04	2.852(14)	159.0	1+x,y,z
2	N(6)-H(6D) ···O(102)	2.22	3.106(15)	142.0	1+x, y, z
	N(7)-H(7E) ···O(103)	1.99	2.960(14)	165.0	1+x, y, z
3	N(3)-H(3A) S(2)	2.602	3.421	153.56	$2-x, \frac{1}{2}+y, \frac{1}{2}-z$

Table S4: Continuous SHAPE analysis of **1-3** to measure deviation from ideal seven coordinate geometries.

Complex	HP-7	HPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
1	33.840	24.231	0.340	8.249	6.481	2.512	24.159
2	33.403	23.223	0.902	8.341	6.607	2.212	23.939
3	33.394	24.703	0.763	7.570	5.788	2.486	23.053

HP-7: Heptagon (D_{7h}); HPY-7: Hexagonal pyramid (C_{6v}); PBPY-7: Pentagonal bipyramid (D_{5h}); COC-7: Capped octahedron (C_{3v}); CTPR-7: Capped trigonal prism(C_{2v}); JPBPY-7: Johnson pentagonal bipyramid (D_{5h}); JETPY-7: Johnson elongated triangular pyramid (C_{3v})

Table S5: Continuous SHAPE analysis of the equatorial plane in **1-3** to measure deviation from ideal five coordinate geometries.

Complex	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY
1	0.254	31.044	36.108	32.318	35.552
2	0.612	30.506	35.827	31.863	34.842
3	0.663	29.237	34.085	30.631	33.260

PP-5: Pentagon (D_{5h}); vOC-5: Vacant octahedron (C_{4v}); TBPY-5: Trigonal bipyramid (D_{3h}); SPY-5: Spherical square pyramid (C_{4v}); JTBPY-5: Johnson trigonal bipyramid (D_{3h})

Table S6: D(experimental) values of reported PBP Ni(II) complexes along with contribution from first three triplet excited states.

Compound	SHAPE	Dexp	Contribution of excited triplet states to			Ref
	PP-5	(cm^{-1})	$D(cm^{-1})$			
			1 st	2^{nd}	3 rd	
[Ni(L3)(NO ₃)(CH ₃ OH)]NO ₃	0.174	-12.5	-91.1	36.4	35.7	11
[Ni(L2)(H ₂ O) ₂](NO ₃) ₂ .2H ₂ O	0.403	-13.9	-66.2	22.5	23.2	10
$[Ni(L4)](ClO_4)_2$	0.875	-12.8	-23.1	0.0	-1.4	12
$[Ni(L5)Cl_2]$	1.212	-6.0	-49.4	21.6	19.7	13
[Ni(L6)].H ₂ O	1.252	-8.5	-	_	_	14

L3= 2,6-diacetylpyridine bis-(4-phenyl)benzohydrazide; L4=3,12-bis(2-methylpyridine)-3,12,18 -triaza-6,9-dioxabicyclo[12.3.1]octadeca-1,14,16-triene;L5=3,12,18-triaza-6,9-dioxabicyclo[12. 3.1]octadeca-1(18),14,16-triene; L6=3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octade ca-1,14,16triene-3,12-diacetic acid Table S7: CASSCF-NEVPT2 calculated contribution of different excited states in compound **1** towards D and E

Block	Multiplicity	Root	D	Ε
0	3	0	0	0
0	3	1	-93.603	0
0	3	2	20.552	-19.97
0	3	3	18.289	17.639
0	3	4	1.27	-1.031
0	3	5	1.543	1.366
0	3	6	1E-3	0
0	3	7	0.065	0.065
0	3	8	0.034	-0.034
0	3	9	0	0
1	1	0	0.056	0
1	1	1	0	0
1	1	2	18.867	0
1	1	3	-6.473	6.465
1	1	4	-6.188	-6.179
1	1	5	0.025	0
1	1	6	-0.103	-0.102
1	1	7	-0.208	0.208
1	1	8	0	0
1	1	9	0.058	0
1	1	10	-1.475	-1.478
1	1	11	-0.056	-0.032
1	1	12	-1.239	1.258
1	1	13	1.087	0.019
1	1	14	1E-3	0

Table S8: CASSCF-NEVPT2 calculated contribution of different excited states in compound **2** towards D and E

Block	Multiplicity	Root	D	E
0	3	0	0	0
0	3	1	-69.445	0.011
0	3	2	22.598	-19.523
0	3	3	20.558	17.496
0	3	4	1.301	-0.492
0	3	5	0.741	0.191
0	3	6	0.007	-1E-3
0	3	7	0.04	0.032
0	3	8	0.042	-0.036
0	3	9	-1E-3	0
1	1	0	0.03	0
1	1	1	0	0
1	1	2	17.076	0
1	1	3	-6.782	6.728
1	1	4	-6.639	-6.608
1	1	5	0.002	0
1	1	6	-0.158	-0.14
1	1	7	-0.324	0.278
1	1	8	-0.002	-1E-3
1	1	9	0.011	1E-3
1	1	10	0.974	-0.004
1	1	11	0.58	-0.011
1	1	12	-1.162	-1.184
1	1	13	-1.127	1.116
1	1	14	0	0

Table S9: CASSCF-NEVPT2 calculated contribution of different excited states in compound **3** towards D and E

Block	Multiplicity	Root	D	Ε
0	3	0	0	0
0	3	1	-60.987	-0.011
0	3	2	21.346	-17.43
0	3	3	19.698	15.528
0	3	4	0.851	-0.447
0	3	5	0.409	0.102
0	3	6	0.039	0.021
0	3	7	0.027	0.025
0	3	8	0.03	-0.03
0	3	9	-1E-3	0
1	1	0	0.03	-1E-3
1	1	1	0	0
1	1	2	16.557	-1E-3
1	1	3	-6.765	6.622
1	1	4	-6.621	-6.511
1	1	5	1E-3	0
1	1	6	-0.162	-0.114
1	1	7	-0.238	0.243
1	1	8	-1E-3	0
1	1	9	0.003	0.009
1	1	10	0.401	-0.002
1	1	11	0.758	-0.114
1	1	12	-0.746	-0.659
1	1	13	-1.026	0.726
1	1	14	1E-3	0

Table S10: CASSCF-NEVPT2 calculated contribution of different excited states in [Ni(L3)(NO₃)(CH₃OH)]NO₃ towards D and E

Block	Multiplicity	Root	D	Ε
0	3	0	0	0
0	3	1	-91.149	-0.289
0	3	2	36.4	-31.014
0	3	3	35.745	28.838
0	3	4	0.799	0.475
0	3	5	0.516	-0.482
0	3	6	0.326	-0.188
0	3	7	0.002	0.002
0	3	8	0.025	-0.016
0	3	9	0.016	0.006
1	1	0	-0.015	0.017
1	1	1	-0.014	0.014
1	1	2	8.478	-2.132
1	1	3	-7.567	6.973
1	1	4	0.886	-4.925
1	1	5	-0.025	-0.024
1	1	6	-0.052	0.038
1	1	7	-0.443	-0.312
1	1	8	-0.379	0.18
1	1	9	-0.056	0.042
1	1	10	-1.201	0.897
1	1	11	-0.739	-1.033
1	1	12	-0.339	0.334
1	1	13	1.933	-0.098
1	1	14	0	0