

Supporting Information (SI) for:

Combined Experimental and Theoretical  
Investigation of the Origin of Magnetic Anisotropy  
in Pentagonal Bipyramidal Isothiocyanato Co(II),  
Ni(II) and Fe(III) Complexes With Quaternary  
Ammonium-functionalized 2,6-diacetylpyridine  
Bisacylhydrazone

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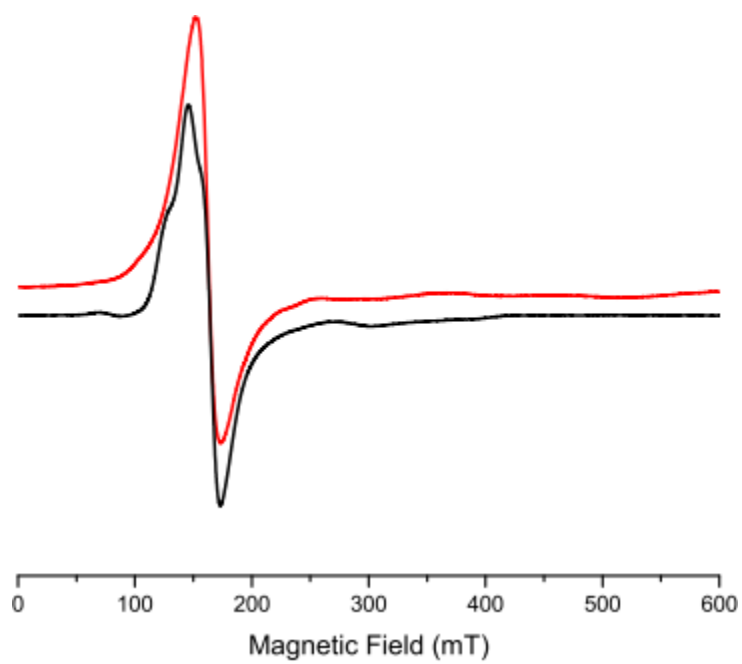
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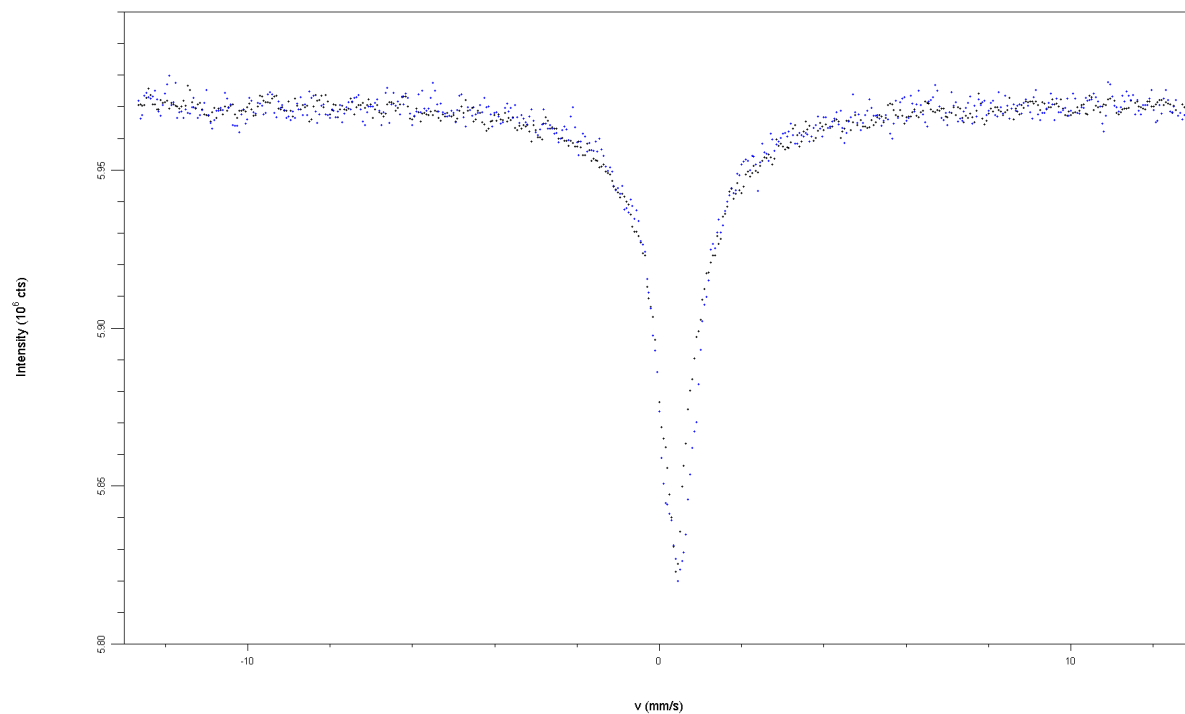
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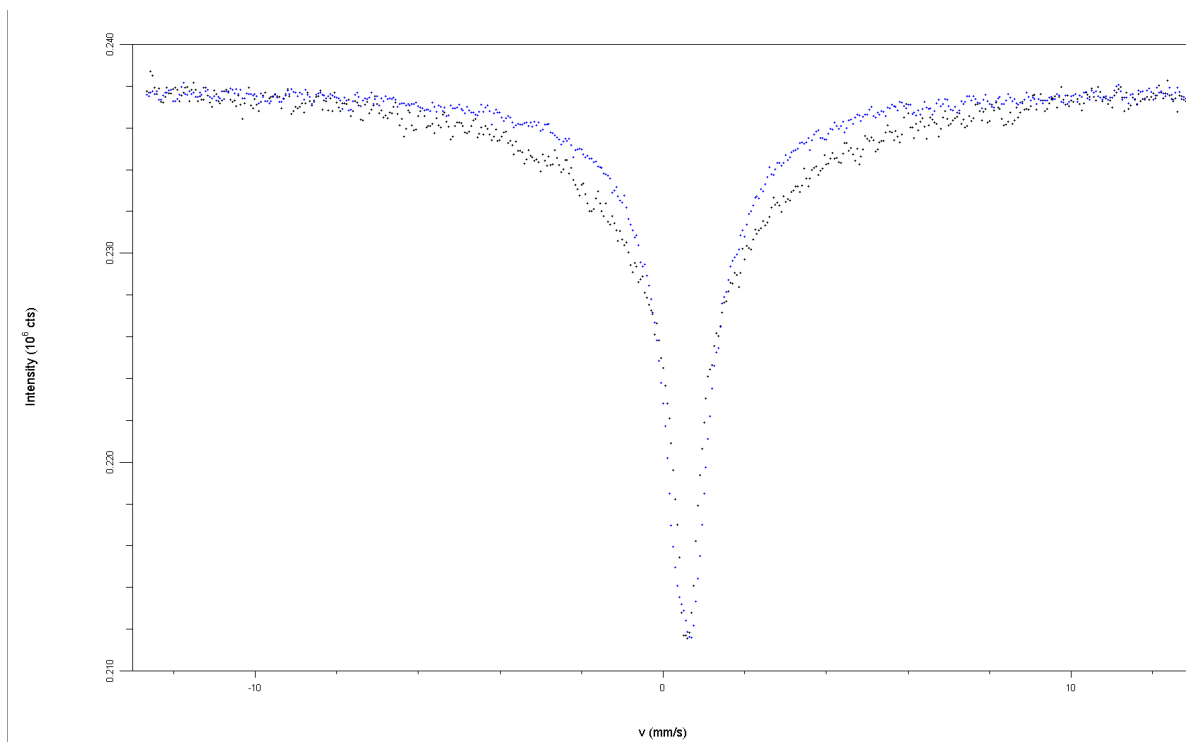
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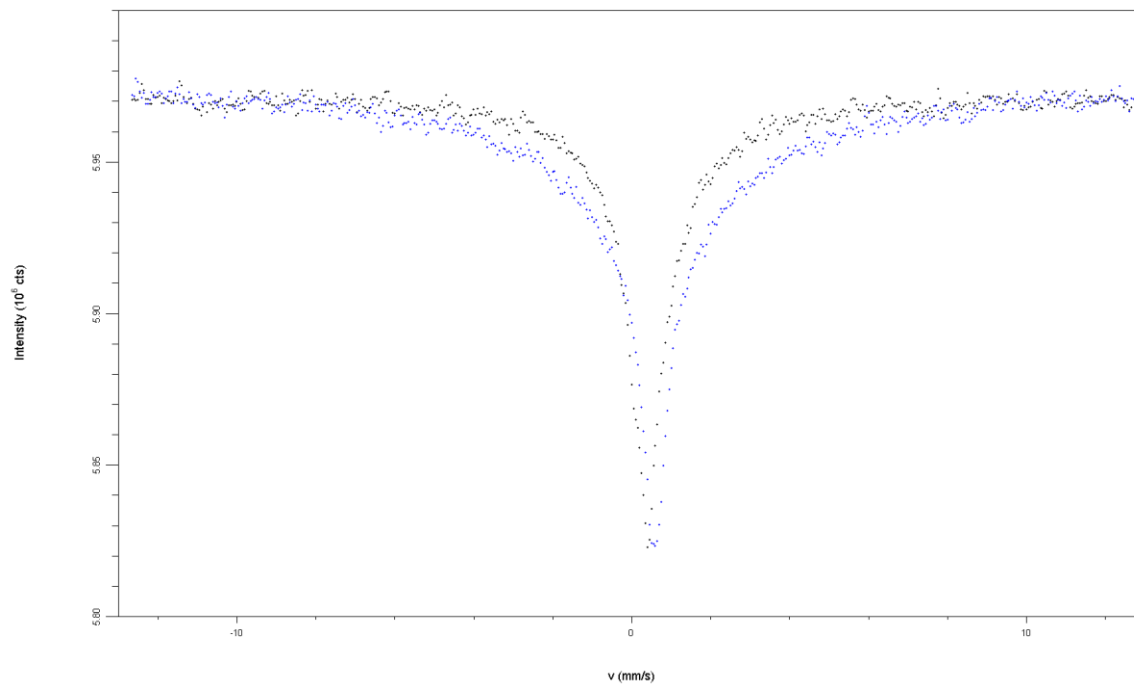
**Figure S1:** Powder X-band EPR spectra of complexes 1 (red line) and 2 (black line).



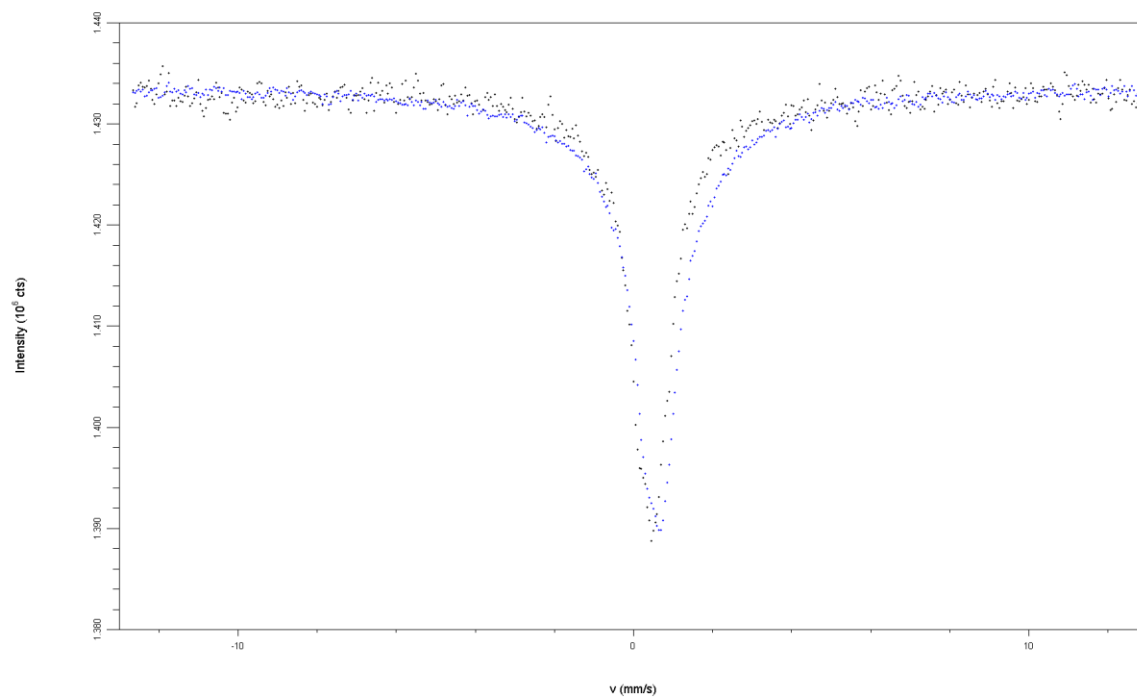
**Figure S2:** Comparison of normalized  $^{57}\text{Fe}$  Mössbauer spectra of Complex **3** (black dots) and Complex **4** (blue dots) recorded at 295K



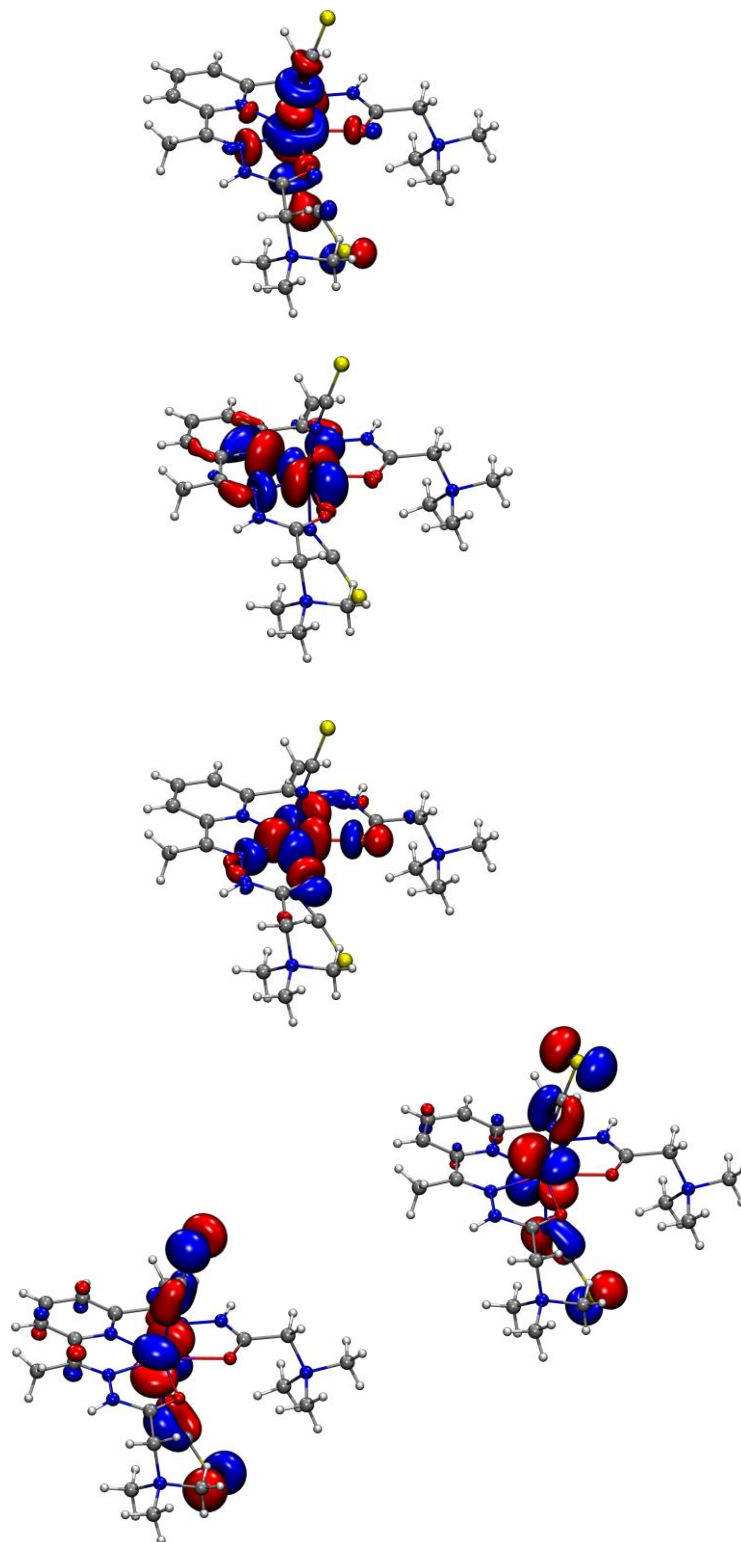
**Figure S3:** Comparison of normalized  $^{57}\text{Fe}$  Mössbauer spectra of Complex **3** (black dots) and Complex **4** (blue dots) recorded at 4K



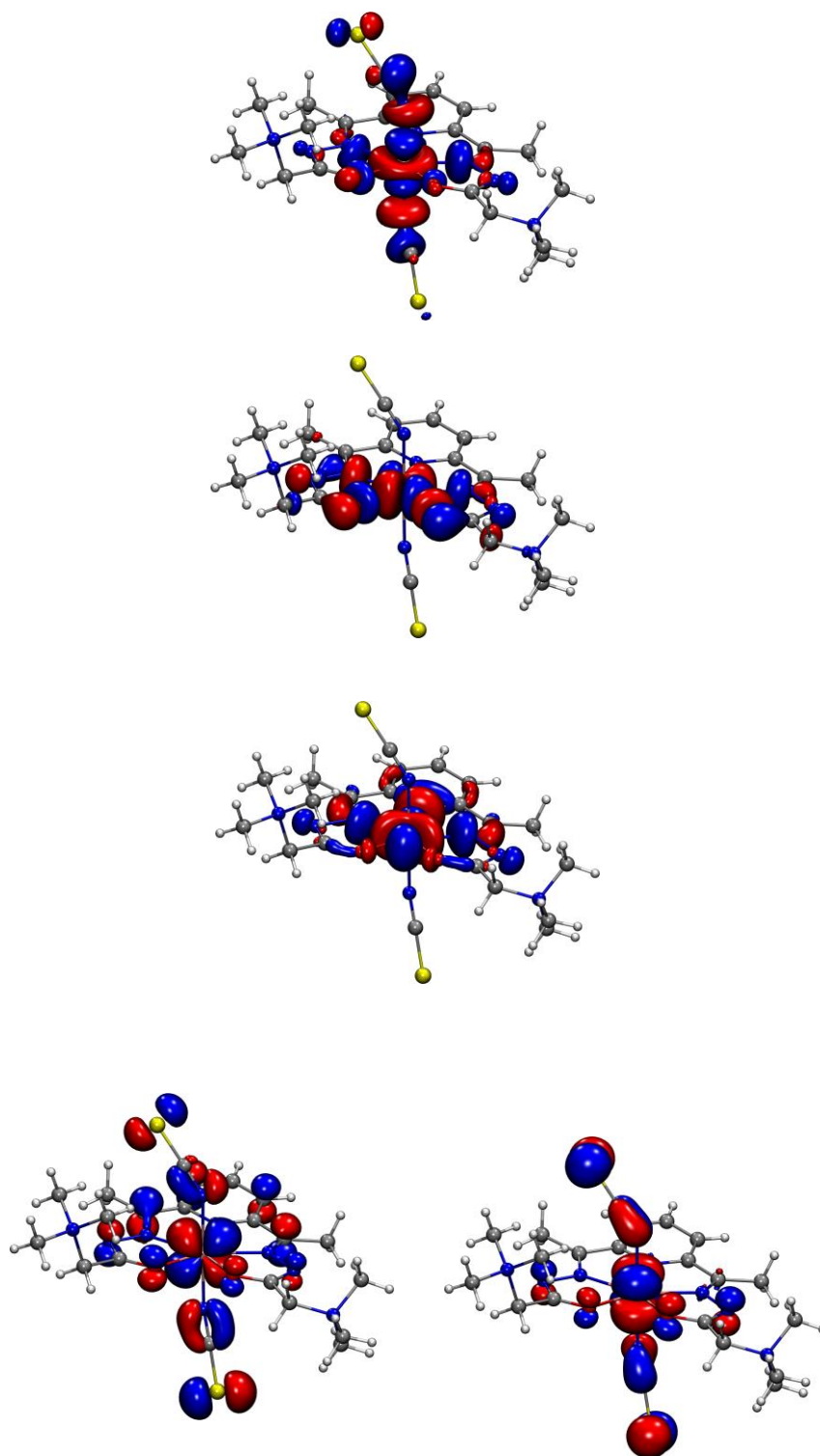
**Figure S4:** Comparison of normalized  $^{57}\text{Fe}$  Mössbauer spectra of Complex **3** recorded at 295K (black dots) and recorded at 4K (blue dots)



**Figure S5:** Comparison of normalized  $^{57}\text{Fe}$  Mössbauer spectra of Complex 4 recorded at 295K (black dots) and recorded at 4K (blue dots)

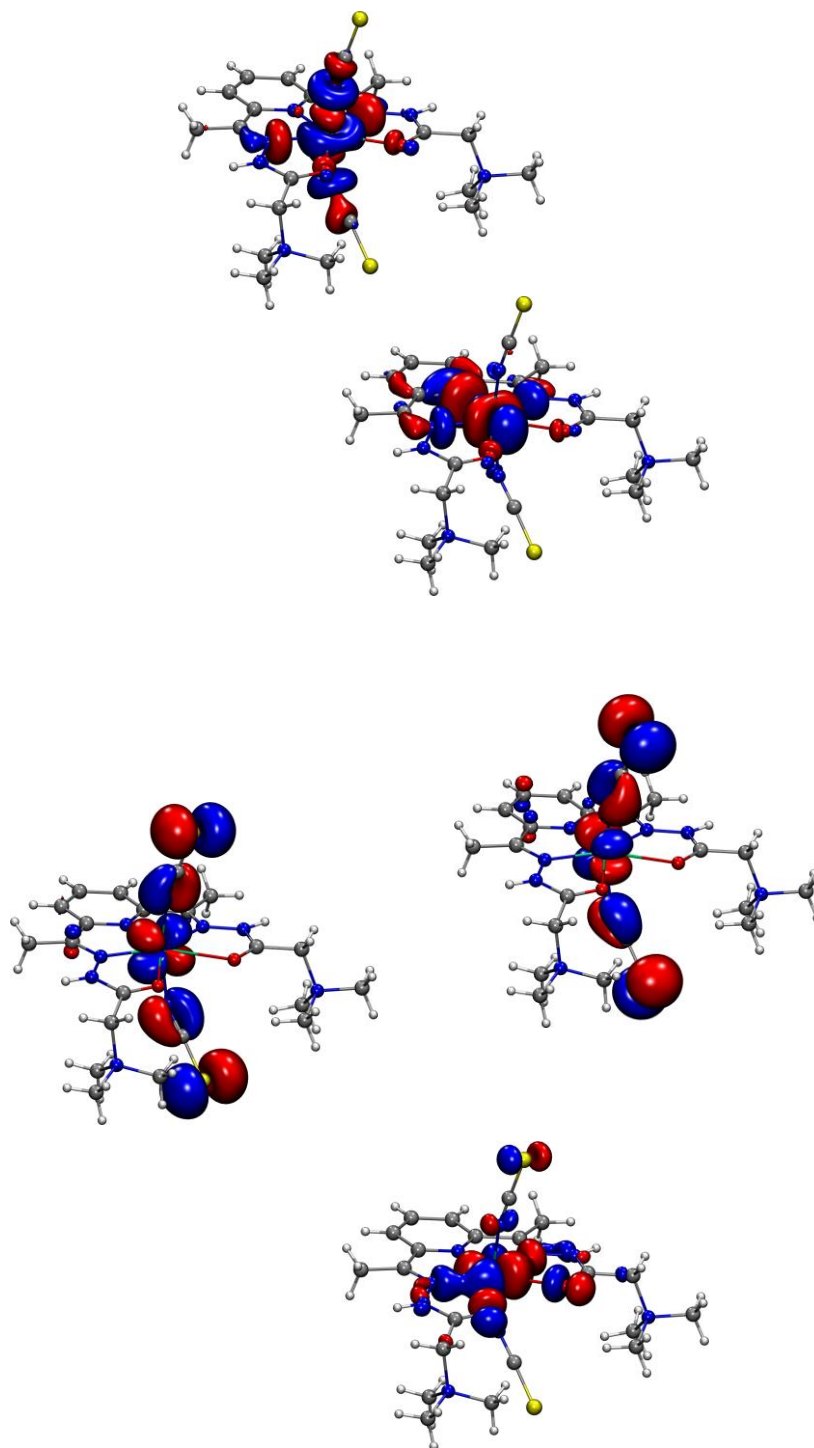


**Figure S6** Kohn-Sham molecular orbitals with dominant metal d character for Co(II) complex **1** (iso-value 0.03 a.u.) generated in an average of configuration (AOC) calculations at ZORA-OPBE(COSMO-water)/TZP level of theory



**Figure S7** Kohn-Sham molecular orbitals with dominant metal d character for Fe(III) complex **3** (iso-value 0.03 a.u.) generated in an average of configuration (AOC) calculations at ZORA-OPBE(COSMO-water)/TZP level of theory





**Figure S8** Kohn-Sham molecular orbitals with dominant metal d character for Ni(II) complex **5** (iso-value 0.03 a.u.) generated in an average of configuration (AOC) calculations at ZORA-OPBE(COSMO-water)/TZP level of theory

**Table S1** Calculated principal components of g-tensor within CASSCF+NEVPT2 approach for PBPY-7 **1-5** compounds

Complex	M	$g_x$	$g_y$	$g_z$	$g_{iso}$
<b>1</b>	Co(II)	1.994	2.371	2.415	2.260
<b>2</b>	Co(II)	1.999	2.336	2.362	2.233
<b>3</b>	Fe(III)	2.000	2.000	2.000	2.000
<b>4-1*</b>	Fe(III)	2.002	2.002	2.002	2.002
<b>4-2*</b>	Fe(III)	2.002	2.002	2.002	2.002
<b>5</b>	Ni(II)	2.224	2.266	2.343	2.278

\*Two independent heptacoordinated Fe(III) species were calculated

**Table S3.** Comparison of calculated (BS-DFT) and experimental magnetic exchange coupling between paramagnetic centers in **2** and **4**; values are given in  $\text{cm}^{-1}$ .

	$J_{\text{PBPY7-T4}}$ ( <b>2</b> )	$J_{\text{PBPY7-PBPY7}}$ ( <b>4</b> )	$J_{\text{PBPY7-OC6}}$ ( <b>4</b> )
Exp.	-0.02	-0.02	-0.03
Calc.	-0.08	-0.02	-0.21

The exchange coupling constant  $J$  was calculated within broken symmetry DFT formalism<sup>1–5</sup> according to the Yamaguchi approach.<sup>6</sup> All calculations were performed with the ORCA program package (version 4.0.1.2) using increased integration grids (Grid5). Scalar relativistic effects were considered at the ZORA level. B97-D functional,<sup>7</sup> proven to be good for this problem,<sup>8</sup> and ZORA-def2-TZVP basis set for all atoms have been used. The resolution of the identity (RI) approximation in the Split-RI-J variant with the scalar relativistically recontracted SARC/J Coulomb fitting sets has been used. CPCM(water) model was employed in order to approximately simulate the environmental effects in the crystal lattice of charged complexes.<sup>9</sup>

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**Table S3.** Transition energies ( $\Delta E$ ,  $\text{cm}^{-1}$ ) and individual contributions of excited states to D and E ZFS parameters ( $\text{cm}^{-1}$ ): for compound **1** (CASSCF(7, 5)+NEVPT2) (lowest 9 doublet and 9 quartet excited states)

Mult	Root	$\Delta E$ , $\text{cm}^{-1}$	D	E
4	0	0.0	0	0
4	1	2152.0	3.2	-2.8
4	2	2366.8	0.7	1.0
4	3	4403.4	18.3	17.9
4	4	5122.6	14.6	-14.2
4	5	11771.6	0.0	0.0
4	6	13339.5	0.0	0.0
4	7	19897.2	0.0	0.0
4	8	21871.1	0.1	-0.1
4	9	22181.7	0.1	0.1
2	0	12445.5	0.0	0.0
2	1	13882.9	0.0	0.0
2	2	17629.1	3.9	0.0
2	3	18563.6	0.0	0.0
2	4	19758.9	-1.0	0.9
2	5	20020.4	-1.5	-1.4
2	6	20528.8	-0.2	-0.1
2	7	20583.6	-0.6	0.6
2	8	20625.9	8.8	0.0
2	9	21932.3	0.0	0.0

**Table S4.** Transition energies ( $\Delta E$ ,  $\text{cm}^{-1}$ ) and individual contributions of excited states to D and E ZFS parameters ( $\text{cm}^{-1}$ ): for compound **2** (CASSCF(7, 5)+NEVPT2) (lowest 9 doublet and 9 quartet excited states)

Mult	Root	$\Delta E$ , $\text{cm}^{-1}$	D	E
4	0	0.0	0	0
4	1	2809.7	1.4	-0.7
4	2	2960.9	0.5	0.3
4	3	5070.4	16.3	14.6
4	4	5498.2	14.3	-13.0
4	5	13333.8	0.0	0.0
4	6	14562.6	0.0	0.0
4	7	20933.2	0.0	0.0
4	8	22623.2	0.2	-0.1
4	9	22789.8	0.2	0.1
2	0	12457.5	0.0	0.0
2	1	13598.2	0.0	0.0
2	2	17829.9	2.7	0.0
2	3	18472.2	0.0	0.0
2	4	20452.8	-1.2	0.4
2	5	20621.1	-1.5	-0.6
2	6	21120.1	-0.1	-0.1
2	7	21127.4	0.0	0.3
2	8	20599	10.1	0.0
2	9	22516.8	0.0	0.0

**Table S5.** Transition energies ( $\Delta E$ ,  $\text{cm}^{-1}$ ) and individual contributions of excited states to D and E ZFS parameters ( $\text{cm}^{-1}$ ): for compound **3** (CASSCF(5, 5)+NEVPT2)

Mult	Root	$\Delta E$ , $\text{cm}^{-1}$	D	E
6	0	0.0	0	0
4	0	18600.0	-0.9	-0.9
4	1	19090.5	-0.8	0.8
4	2	28172.3	0.0	0.0
4	3	28290.8	0.0	0.0
4	4	28858.4	0.0	0.0
4	5	29306.7	0.3	0.0
4	6	29925.3	0.0	0.0
4	7	30464.5	0.0	0.0
4	8	30605.3	0.0	0.0
4	9	32414.7	0.1	0.1
4	10	32682.6	0.0	0.0
4	11	34875.9	2.2	0.0
4	12	34891.3	0.0	0.0
4	13	35774.1	0.0	0.0
4	14	36375.8	0.0	0.0
4	15	43630.8	-0.7	0.7
4	16	44357.6	-0.7	-0.7
4	17	50074.1	0.0	0.0
4	18	50129.8	0.0	0.0
4	19	52057.9	0.0	0.0
4	20	52236.4	0.0	0.0
4	21	52324.4	0.0	0.0

4	22	55451.2	0.0	0.0
4	23	55919.8	0.0	0.0

**Table S6.** Transition energies ( $\Delta E$ ,  $\text{cm}^{-1}$ ) and individual contributions of excited states to D and E ZFS parameters ( $\text{cm}^{-1}$ ): for compound **5** (CASSCF(8, 5)+NEVPT2)

Mult	Root	$\Delta E$ , $\text{cm}^{-1}$	D	E
3	0	0.0	0	0
3	1	6712.3	-63.7	0.0
3	2	8179.0	24.5	-24.5
3	3	9755.2	20.7	20.7
3	4	14077.1	0.8	0.8
3	5	14673.9	0.7	-0.7
3	6	15232.9	0.0	0.0
3	7	26001.6	0.0	0.0
3	8	26586.6	0.0	0.0
3	9	28293.6	0.0	0.0
1	0	14965.3	0.0	0.0
1	1	16084.1	0.0	0.0
1	2	22355.8	16.4	0.0
1	3	23552.1	-7.2	7.2
1	4	24880.3	-6.6	-6.6
1	5	28124.8	0.0	0.0
1	6	29308.3	-0.2	-0.2
1	7	30120	-0.2	0.2
1	8	33145.9	0.0	0.0
1	9	35611.3	0.0	0.0
1	10	36210.9	1.8	0.0
1	11	36669.4	0.0	0.0
1	12	37072.5	-1.2	-1.2



1	13	37269.4	-1.0	-1.0
1	14	62860.7	0.0	0.0

**Table S7.** d-Orbitals splitting ( $\text{cm}^{-1}$ ) according to AI-LFT analysis for complexes 1-3, 5

AOs	Co (1)	Co (2)	AOs	Fe (3)	AOs	Ni (5)
$d_{yz}$	0.0	0.0	$0.54 d_{yz} + 0.83 d_{xz}$	0.0	$d_{xy}$	0.0
$d_{xz}$	220	191	$0.84 d_{yz} - 0.55 d_{xz}$	64	$d_{yz}$	393
$d_{xy}$	2197	2863	$d_{x^2-y^2}$	5119	$d_{xz}$	725
$d_{x^2-y^2}$	3464	3907	$d_{xy}$	7377	$d_{x^2-y^2}$	5684
$d_z^2$	8600	9289	$d_z^2$	12336	$d_z^2$	9653

**Table S8.** Multi-determinant wave function of the ground and selected excited states for complexes **1**, **2**, **3** and **5** with heptacoordinated metal center. The computed CI states composition (in %, configurations with contribution larger than 10% are shown).

**Compound 1, ground quartet state**

	87%	13%
$d_{z^2}$	1	1
$d_{x^2-y^2}$	1	2
$d_{xy}$	1	2
$d_{xz}$	2	1
$d_{yz}$	2	1

**3<sup>rd</sup> excited quartet state**

	52%	27%	22%
$d_{z^2}$	1	2	1
$d_{x^2-y^2}$	2	1	1
$d_{xy}$	1	1	2
$d_{xz}$	2	2	1
$d_{yz}$	1	1	2

**4<sup>th</sup> excited quartet state**

	62%	24%	14%
$d_{z^2}$	1	2	1
$d_{x^2-y^2}$	2	1	1
$d_{xy}$	1	1	2
$d_{xz}$	1	1	2
$d_{yz}$	2	2	1

**9<sup>th</sup> excited doublet state**

%	66%	11%
$d_{z^2}$	1	1
$d_{x^2-y^2}$	2	2
$d_{xy}$	0	2
$d_{xz}$	2	2
$d_{yz}$	2	0

**Compound 2, ground quartet state**

	86%	13%
$d_{z^2}$	1	1
$d_{x^2-y^2}$	1	2
$d_{xy}$	1	2
$d_{xz}$	2	1
$d_{yz}$	2	1

**3<sup>rd</sup> excited quartet state**

%	46%	26%	25%
$d_{z^2}$	1	2	1
$d_{x^2-y^2}$	2	1	1
$d_{xy}$	1	1	2
$d_{xz}$	2	2	1
$d_{yz}$	1	1	2

**4<sup>th</sup> excited quartet state**

	56%	24%	18%
$d_{z^2}$	1	2	1
$d_{x^2-y^2}$	2	1	1
$d_{xy}$	1	1	2
$d_{xz}$	1	1	2
$d_{yz}$	2	2	1

**9<sup>th</sup> excited doublet state**

%	58%
$d_{z^2}$	1
$d_{x^2-y^2}$	2
$d_{xy}$	0
$d_{xz}$	2
$d_{yz}$	2

**Compound 3, ground sextet state**

	100%
$d_{z^2}$	1
$d_{xy}$	1
$d_{x^2-y^2}$	1
$d_{yz}$	1
$d_{xz}$	1

**1<sup>st</sup> excited quartet state**

%	81%
$d_{z^2}$	0
$d_{xy}$	1
$d_{x^2-y^2}$	1
$d_{yz}$	1
$d_{xz}$	2

**2<sup>nd</sup> excited quartet state**

	83%
$d_{z^2}$	0
$d_{xy}$	1
$d_{x^2-y^2}$	1
$d_{yz}$	2
$d_{xz}$	1

**12<sup>th</sup> excited quartet state**

%	60%	13%	13%
$d_{z^2}$	1	1	1
$d_{xy}$	2	0	1
$d_{x^2-y^2}$	0	2	1
$d_{yz}$	1	1	2
$d_{xz}$	1	1	0

**16<sup>th</sup> excited quartet state**

%	46%	25%	23%
$d_{z^2}$	2	1	1
$d_{xy}$	1	1	2
$d_{x^2-y^2}$	1	2	1
$d_{yz}$	0	0	1
$d_{xz}$	1	1	0

**17<sup>th</sup> excited quartet state**

%	45%	26%	23%
$d_{z^2}$	2	1	1
$d_{xy}$	1	1	2
$d_{x^2-y^2}$	1	2	1
$d_{yz}$	1	1	0
$d_{xz}$	0	0	1

**Compound 5, ground state**

	100%
$d_{z^2}$	1
$d_{x^2-y^2}$	1
$d_{yz}$	2
$d_{xz}$	2
$d_{xy}$	2

**1<sup>st</sup> excited triplet state**

	100%
$d_{z^2}$	1
$d_{x^2-y^2}$	2
$d_{yz}$	2
$d_{xz}$	2
$d_{xy}$	1

**2<sup>nd</sup> excited triplet state**

	56%	42%
$d_{z^2}$	2	1
$d_{x^2-y^2}$	1	2
$d_{yz}$	1	1
$d_{xz}$	2	2
$d_{xy}$	2	2

**3<sup>rd</sup> excited triplet state**

	56%	42%
$d_{z^2}$	2	1
$d_{x^2-y^2}$	1	2
$d_{xy}$	2	2
$d_{xz}$	1	1
$d_{yz}$	2	2