

Magnetic anisotropy in pentagonal bipyramidal complexes of first row transition metal complexes

Filip Vlahović^a, Maja Gruden^b, and Matija Zlatar^c

^a Innovative Centre, Faculty of Chemistry, University of Belgrade, Studentski trg 12–16, 11000 Belgrade, Serbia

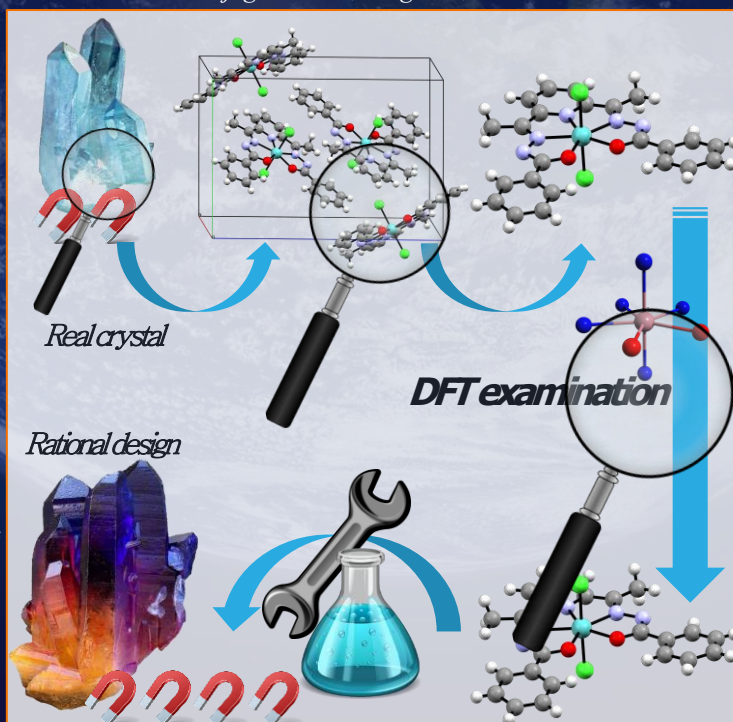
^b University of Belgrade, Faculty of Chemistry, Studentski trg 12-16, Belgrade, Serbia

^c University of Belgrade, Institute of Chemistry, Technology and Metallurgy, ICHTM, Njegoševa 12, Belgrade, Serbia



Introduction

Single-molecule magnets (SMMs) are paramagnetic molecular metal complexes that can retain their magnetization after removal of the magnetic field below a certain temperature. The height of the magnetization reversal barrier depends on the total spin of the system. In the past decade, high magnetic anisotropy, characterized by the zero-field splitting parameter, D , has been considered to be the most important for high-performance SMMs. Magnetic anisotropy is influenced by multiple factors such as coordination number, molecular symmetry, ligand-field strength, and spin-orbit coupling. Therefore, design, control, and fine-tuning of magnetic anisotropy is a challenging task. In present study we work on 26 seven-coordinate high-spin first row transition metal (TM), and utilize two DFT methods (SP-DFT and LF-DFT) in order to accurately describe and predict the magnetic anisotropy.



Conclusion

In present study we established and proposed a theoretical procedure for accurate geometrical optimization of all 26 investigated seven-coordinate high-spin first row TM complexes, and thus overcame all obstacles concerning this task. In order for our work to have benchmarking character, we have utilized various DFT flavours and different computational conditions in every theoretical step of research. After obtaining the best geometry of investigated complexes, we carried out theoretical calculation of ZFS parameters D and E . Our preliminary results show really good and consistent performance of LF-DFT method, in contrast to CP-DFT, which is considered as gold standard for most problems in this field. Our results must be considered with caution, since we did not cover all investigated metal ions... More scientific results are on the way!

Geometrical parameters

Geometry deviation relative to the perfect PBPY-7 coordination environment

Crystal structure / DFT flavours:	Crystal	LDA	BP86	PBE	BLYP	B3LYP	M06L
[V ^{III} (H ₂ N ₃ O ₂ Bz)(Cl) ₂] ⁺	0.481	0.326	0.361	0.364	0.390	0.377	0.380
[V ^{III} (N ₃ O ₂ Bz)(MeOH) ₂] ⁺	0.048	0.141	0.138	0.105	0.099	0.092	0.083
[V ^{III} (HN ₃ O ₂ Bz)(NCS) ₂] ⁺	0.188	0.064	0.048	0.047	0.048	0.039	0.049
[Cr ^{III} (HN ₃ O ₂ BzOMe)(Cl) ₂]	0.467	0.608	0.855	0.789	0.472	0.452	0.361
[Fe ^{III} (N ₃ O ₂ CH ₂ NMe ₃)(NCS) ₂] ⁺	0.211	0.210	0.227	0.194	0.202	0.195	0.150
[Mn ^{II} (MeOCHN ₃ O ₂ Bz ₂)(H ₂ O)(EtOH)] ⁺	1.122	1.310	0.557	0.474	0.489	0.475	0.448
[Fe ^{II} (H ₂ N ₃ O ₂ NH ₂)(Cl) ₂]	0.685	0.386	0.394	0.477	0.459	0.496	0.593
[Fe ^{II} (H ₂ N ₃ O ₂ Bz)(H ₂ O)(MeOH)] ²⁺	0.733	0.650	0.272	0.234	0.295	0.249	0.283
[Fe ^{II} (H ₂ N ₃ O ₂ Bz)Cl ₂]	0.914	0.469	0.433	0.492	0.502	0.495	0.588
[Fe ^{II} (H ₂ N ₃ O ₂ biBz)(MeOH)Cl] ⁺	0.690	0.441	0.515	0.498	0.496	0.546	0.570
[Co ^{II} (H ₂ N ₃ O ₂ CH ₂ NMe ₃)(NCS) ₂] ²⁺	0.283	0.479	0.541	0.494	0.645	0.583	0.370
[Co ^{II} (MeOCHN ₃ O ₂ Bz)(H ₂ O)(EtOH)] ⁺	0.132	0.671	0.303	0.292	0.283	0.361	0.125
[Co ^{II} (N ₃ O ₂ BzOH)(MeOH) ₂]	0.240	0.344	0.268	0.181	0.295	0.321	0.200
[Co ^{II} (H ₂ N ₃ O ₂ BzOH)(NCS)(MeOH)] ⁺	0.211	0.239	0.243	0.275	0.326	0.422	0.201
[Co ^{II} (H ₂ N ₃ O ₂ BzOH)(NCS) ₂]	0.464	0.319	0.269	0.252	0.326	0.176	0.280
[Co ^{II} (H ₂ N ₃ O ₂ Bz)(SCN) ₂]	0.250	0.342	0.214	0.196	0.249	0.336	0.159
[Co ^{II} (N ₃ O ₂ Bz)(H ₂ O) ₂]	0.341	1.408	0.593	0.856	0.521	0.640	0.244
[Co ^{II} (H ₂ N ₃ O ₂ biBz)(MeOH)(NO ₂) ⁺	0.202	0.355	0.400	0.400	0.356	0.508	0.414
[Co ^{II} (N ₃ O ₂ Bz)(imidazole) ₂]	0.396	0.119	0.095	0.080	0.130	0.175	0.129
[Co ^{II} (H ₂ N ₃ O ₂ NH ₂)(NCS) ₂]	0.312	0.299	0.099	0.136	0.262	0.257	0.271
[Ni ^{II} (H ₂ N ₃ O ₂ CH ₂ NMe ₃)(NCS) ₂] ²⁺	1.009	1.209	1.009	1.298	1.345	0.816	0.953
[Ni ^{II} (H ₂ N ₃ O ₂ NH ₂)(H ₂ O)] ²⁺	0.710	4.803	5.500	5.104	5.144	4.528	0.333
[Ni ^{II} (H ₂ N ₃ O ₂ NH ₂)(NCS) ₂]	0.454	0.955	0.719	0.767	0.849	0.608	0.896
[Ni ^{II} (H ₂ N ₃ O ₂ NH ₂)(imidazole) ₂] ⁺	0.364	0.955	0.648	0.611	0.767	0.471	0.407
[Ni ^{II} (H ₂ N ₃ O ₂ Bz)(SCN) ₂]	0.799	1.138	0.958	1.008	1.102	0.690	0.761
[Ni ^{II} (H ₂ N ₃ O ₂ biBz)(MeOH)(NO ₂) ⁺	0.341	1.282	0.782	0.931	0.721	0.527	0.427

LF-DFT (ADF-2017.01, ZORA, SR, TZP-D, COSMO(water)); CP-DFT (Orca-5.0.3, SR, ZORA-def2-TZVP(f) – X-ray geometry)

ZFS parameters obtained by DFT methods

ZFS parameters (D and E) in cm⁻¹

DFT flavours/ geometry	OPBE-X-ray	PBE0-X-ray	LF-DFT	
			OPBE-opt	PBE0-opt
[Co ^{II} (H ₂ N ₃ O ₂ CH ₂ NMe ₃)(NCS) ₂] ²⁺	D=+30.9 E=+0.8	D=+54.7 E=+1.8	D=+32.9 E=+0.9	D=+60.5 E=+2.7
[Co ^{II} (N ₃ O ₂ BzOH)(MeOH) ₂]	D=+28.7 E=+1.7	D=+70.01 E=+5.5	D=+26.2 E=+1.0	D=+68.2 E=+4.5
[Co ^{II} (H ₂ N ₃ O ₂ BzOH)(NCS)(MeOH)] ⁺	D=+30.4 E=0.4	D=+51.0 E=+1.7	D=+29.5 E=+0.8	D=+54.6 E=+1.8
[Co ^{II} (H ₂ N ₃ O ₂ BzOH)(NCS) ₂]	D=+31.4 E=+1.3	D=+53.9 E=+3.0	D=+30.3 E=+1.1	D=+56.8 E=+2.8
CP-DFT				
DFT flavours/ geometry	BP86	B3LYP	M06-2X	Exp.
[Co ^{II} (H ₂ N ₃ O ₂ CH ₂ NMe ₃)(NCS) ₂] ²⁺	D=+6.1 E=0.3	D=+7.2 E=0.3	D=+14.7 E=0.5	D=+30.01 E=0
[Co ^{II} (N ₃ O ₂ BzOH)(MeOH) ₂]	D=+11.8 E=0.1	D=+16.7 E=0.3	D=+22.1 E=1.5	D=+43.1 E=3.3
[Co ^{II} (H ₂ N ₃ O ₂ BzOH)(NCS)(MeOH)] ⁺	D=+9.0 E=0.3	D=+11.9 E=0.1	D=+46.1 E=0.7	D=+41.5 E=1.5
[Co ^{II} (H ₂ N ₃ O ₂ BzOH)(NCS) ₂]	D=+8.8 E=0.2	D=+7.9 E=0.3	D=+12.6 E=0.3	D=+38.8 E=2.1

Crystal structure axial angle deviation (δ°)

DFT flavours:	LDA	BP86	PBE	BLYP	B3LYP	M06L
Absolute total deviation:	5.491	3.118	3.408	3.231	2.971	0.77

Chemical bonds in the first coordination sphere deviation (\AA)

DFT flavours:	LDA	BP86	PBE	BLYP	B3LYP	M06L
Absolute total deviation:	0.092	0.066	0.067	0.061	0.04	0.04