Project “Molecular Magnetism”.

I.Motivation

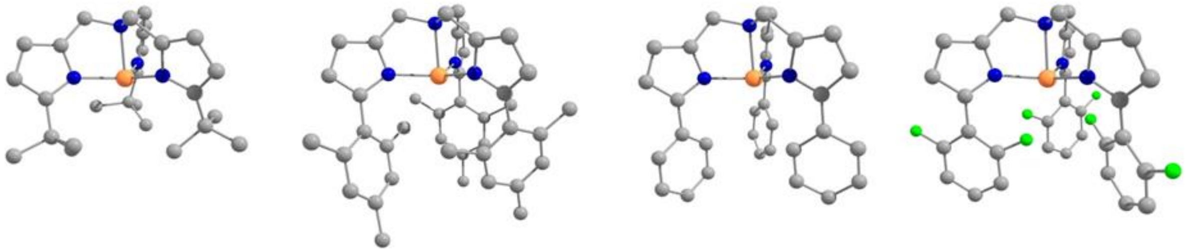
Molecular magnetism is a multidisciplinary field that combines synthesis of molecules with desired magnetic properties and theoretical analysis aiming at mechanistic understanding of the relation of these properties with the electronic structure. Spectacular advances in the development and implementation in the program ORCA of spin-dependent relativistic correlated electronic structure methods for larger systems by Prof. Dr. Frank Neese and his developer team supplied the infrastructure and serves as a firm theoretical basis for this project. The combination of experiment and theory on a one-to-one basis allows to *both interpret and to predict* (rationally design) magnetic properties of target magnetic materials. Molecular magnetism has a big impact on closely related disciplines such as molecular electronics and chemical reactivity (homogeneous and heterogeneous catalysis). The latter has been inspired by the action of transition metal spin centers at the active sites in enzymes such as the spitting of water on a four nuclear mixed-valence manganese complex (Photosystem II) and oxygen and hydrogen atom transfer in heme and non-heme high-valence iron enzymes leading to molecules for energy storage. All this motivated the creation in 2013 of a group on molecular magnetism at the institute. Basic tools in the work on this project have been: i) computational protocols allowing to extract magnetic and spin-Hamiltonian (SH) parameters from ab intio correlated wavefunctions [1a], and ii) an ab initio based ligand field theory (AILFT) that allows to relate the magnetic parameters with the nature of the metal-ligand bonds and the complex geometries [1b].

II. Molecular Magnetism

Open d- or f-shell transition metal or lanthanides and actinides in complexes give rise to a unique response to an external magnetic field governed by the preferred alignments of their magnetic moments. This property is termed magnetic anisotropy. In axial symmetry this anisotropy is described by one parameter D which quantifies the zero-field splitting of the 2S+1 sublevels M ($-S \leq M \leq S$) of the spin S ($E=DM^2$) of the non-relativistic ground state. Magnetic anisotropy arises from coupling between orbital and spin angular momenta. Below a given temperature (called the blocking temperature, T_B) the resulting total angular momentum and its magnetization induced by an external magnetic field may persists after switching off the field. The specific life-time of this magnetic state -the relaxation time depends on the magnitude of the orbital angular momentum and its coupling to its dissipative surrounding (thermal bath). Orbital momenta are maximal in atoms and ions with orbitally degenerate ground states, such as Fe^{I} $^4F(d^7)$ or Fe^{II} $^2D(d^6)$. However, because of their spherical symmetry, such orbital moments are isotropic. Anisotropic magnetic moments are intrinsic for molecules possessing axial (four of threefold) symmetries, which in addition, are in orbitally degenerate or nearly-denerate ground states. Spin-orbit coupling introduces atomic like orbital moments which couple with the spin and this leads to an entirely anisotropic magnetization (Ising anisotropy). This magnetization is maximal along the axis of quantization (the easy axis, D<0) and (in weak magnetic fields) very small in directions perpendicular to it.

The project focusses on magnetic properties of transition metal complexes with open d-shells. Open d- or f-shell transition metal or a lanthanide complexe can give rise to a unique response to an external magnetic field governed by the preferred alignments of their magnetic moments. This property is termed magnetic anisotropy. In axial symmetry this anisotropy is described by one parameter D which quantifies the zero-field splitting of the 2S+1 sublevels M ($-S \leq M \leq S$) of the spin S ($E=DM^2$) within a given electronic state (normally the non-relativistic ground state). Magnetic anisotropy arises from coupling between orbital and spin angular momenta. Below a given temperature (called the blocking temperature, T_B) the resulting total angular momentum and its magnetization induced by an external magnetic field may persists after switching off the field. The specific life-time of this magnetic state -the relaxation time depends on the magnitude of the orbital angular momentum and its coupling to its dissipative surrounding (thermal bath). Orbital momenta are maximal in atoms and ions with orbitally degenerate ground states, such as Co(II) ^{4}F or Fe(II) ^{2}D. However, because of the spherical symmetry, such orbital moments are isotropic and do not create magnetic anisotropies. Anisotropic magnetic moments are intrinsic for molecules possessing axial four of threefold symmetries, which in addition, are in orbitally degenerate ground states. First order spin-orbit coupling in such systems introduces atomic like orbital moments which couple with the spin and this leads to an entirely anisotropic magnetization. This magnetization is maximal along the axis of quantization (the easy axis, $D<0$) and (in weak magnetic fields) very small in directions perpendicular to it (Ising type anisotropy). A series of pseudo-tetrahedral Fe(II) complexes of this type has been theoretically predicted [1] by first principles calculations and synthesized and magnetically characterized [2,3] at about the same time (see Figure 1). These were shown to display slow relaxation of the magnetization and were termed single ion magnets (SIM). These discoveries opened a new field in magneto chemistry. The ultimate goal of the studies carried out within this project is to increase the blocking temperature and the relaxation time making such systems potential candidates for magnetic memory devices. Systems with magnetically bi stable ground states in molecules well isolated from their dissipative surroundings can also display quantum coherence and are therefore of potential interest in future quantum computers.

Based on the infrastructure given by the development and implementation of multi reference electronic structure methods in the ORCA program by Prof. Frank Neese and his group, we developed and tested computational protocols for first principles computations of the magnetic and spectroscopic properties of SIM which allow to both interpret and predict such phenomena [4]. We applied these tools to the interpretation of existing SIM and to assist rational design of novel ones with improved magnetic properties. We studied trigonal four coordinate (Figure 1, [4]) and pseudo linear two coordinate Fe(II) complexes (Figure 2, [5,6]) the latter displaying magnetic anisotropies on unprecedented size.



(Fe^{II}-**1**) [(tpa^{tBu})Fe]$^-$ (Fe^{II}-**2**) [(tpa^{Mes})Fe]$^-$ (Fe^{II}-**3**) [(tpa^{Ph})Fe]$^-$ (Fe^{II}-**4**) [(tpa^{DFP})Fe]$^-$

Figure 1: Molecular structure of the trigonal pyramidal Fe^{II}N$_4$ complexes with derivatives of the trianionic tris(pyrrolyl-α-methyl) amines ligand. Color code: orange (Fe), blue (N), green (F) and gray (C). Hydrogen atoms have been omitted for clarity.

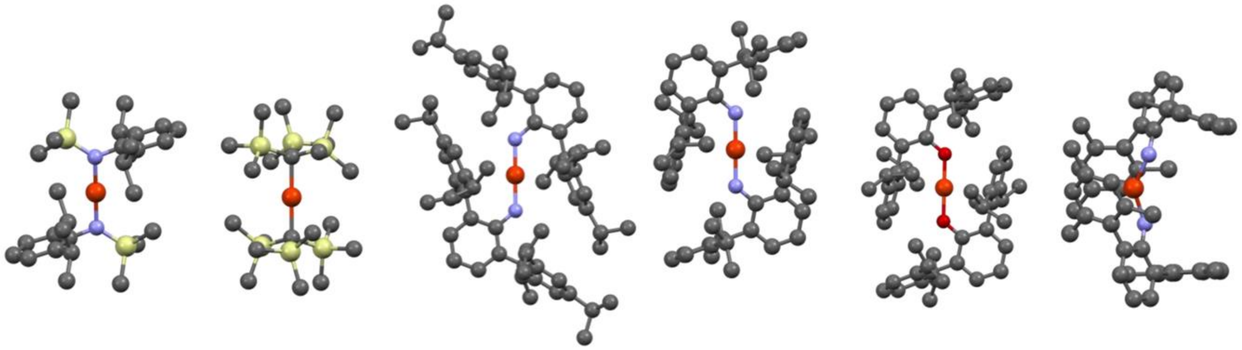


Figure 2. Structure of two-coordinated Fe(II) complexes Fe^{II} from left to right. Orange, yellow, red, blue, and gray spheres represent Fe, Si, O, N, and C atoms, respectively; H atoms have been omitted for the sake of clarity.

A fruitful scientific exchange with our collaborators (Prof.J.Long, Berkeley, USA) culminated in understanding of the magnetic properties of these class of compounds and the first SIM displaying a magnetic hysteresis and magnetic blocking temperature T_B=4K (Figure 3) [7].

Vibronic coupling and molecular magnetism.

Expanding on our expertise on vibronic coupling and the Jahn-Teller effect in transition metal molecular and extended solids [8] we studied the static and dynamic Renner-Teller effects in trigonal pseudo-tetrahedral and pseudo-linear Fe(II) complexes with ^5E non-relativistic ground states, respectively. While being supportive for reactivity, vibronic coupling is not in favor for SIM. Low symmetry distortions of the high-symmetric nuclear configuration causes partial or complete quenching of orbital angular momenta thus reducing the magnetic anisotropy (Figure 3). Suppression of the vibronic coupling is possible when using bulky ligands which enforce ligand rigidity.

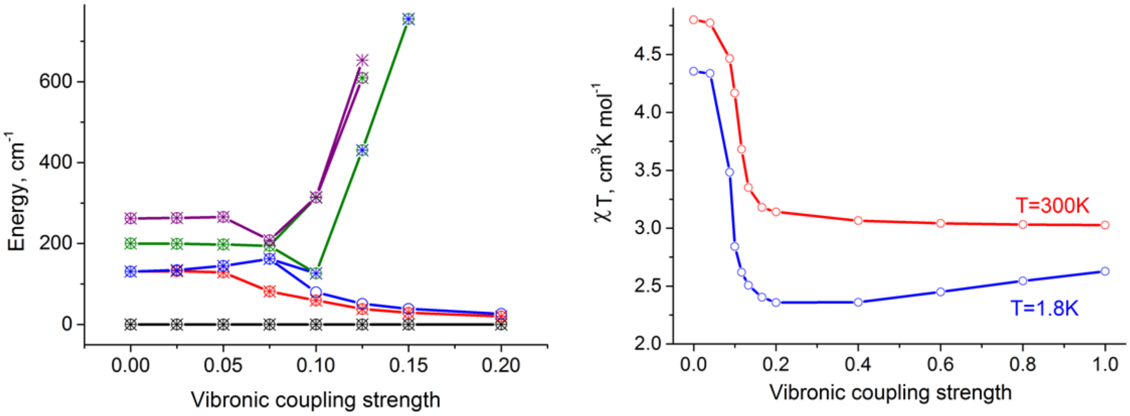


Figure 3. Calculated energy spectra (left) and magnetic susceptibility (right) of the model $Fe(CH_3)_2$ complex as a function of vibronic coupling strength (x-axis: 0 – vibronic coupling is switched off, 1 – fully switched on).

Ligand field theory from first principles – a powerful tool toward chemical insight in magnetism and reactivity

Ligand field theory is an effective Hamiltonian model approaching the electronic multiplets spanned by d^n/f^n configurations of a transition metal/lanthanide complexes by a Hamiltonian matrix with matrix elements depending linearly on the parameters of the ligand field. These are parameters that represent the one- and two-electron parts of the Hamiltonian: metal-ligand bonding [the one-electron 5x5 (d^n)/7x7(f^n) ligand field matrices] and interelectronic repulsion [F_{dd}^2, $F_{dd}^4/F_{ff}^2, F_{ff}^4$, F_{ff}^6, or alternatively Racah parameters $B,C/E^1,E^2,E^3$]. Ligand field parameters have been deduced from a fit to high resolution spectra. Such empirically derived energy quantities were the only source of information about the metal-ligand bond at a time when first principle electronic structure methods were far from practical utility. This phenomenological ligand field model was also employed to relate magnetic properties with the electronic multiplet structure thus yielding first insight into the magnetism in molecules and solids. Following an idea by Prof.Frank Neese, a method was developed, implemented (MatLab) and interfaced with the program ORCA [9,10]. The procedure did allow deducing uniquely the 5x5/7x7 ligand field matrices and the parameters of inter electronic repulsion from one-to-one least square fit to the matrix elements of the Hamiltonian from multireference CASSCF/NEVPT2 *ab initio* calculations. A more detailed information about the metal-ligand bond is possible employing the angular overlap model. In this parameterization, metal-ligand energies of antibonding (implying dative σ or π-dative bonds, e_σ and e_π, respectively assuming positive values) or bonding (σ or π-back bonding, e_σ and e_π -negative) are defined in a frame of optimally aligned metal-ligand d_{z2}-p_z and d_{xz}-p_x,d_{yz}-p_y orbitals. The elements of the ligand field matrix are then expressed in terms of such parameters times angular factors accounting for the positions of the ligands in the metal first coordination sphere. When extracted from a best fit to *ab initio* 5x5/7x7 ligand field matrices, such parameters provide an indispensable tool for:

i) interpreting and understanding numerical results from *ab initio* calculations thus translating such data directly into a chemically transparent language.

ii) to be used as diagnostic tool toward improving the *ab initio* methodology by comparison between sets of ligand field parameters deduced from *ab initio* and from high-resolution spectra.

iii) correlation between metal-ligand bonding parameters and the zero-field splitting did allow establishing magneto-structural correlations which can be directly used in a rational design of SMM.

The power of this *ab initio* based ligand field model is highlighted in Figures 4 (i, and ii) and 5 (iii), respectively.

Achievements of our work on this project have been documented in recent review Ref.[10]

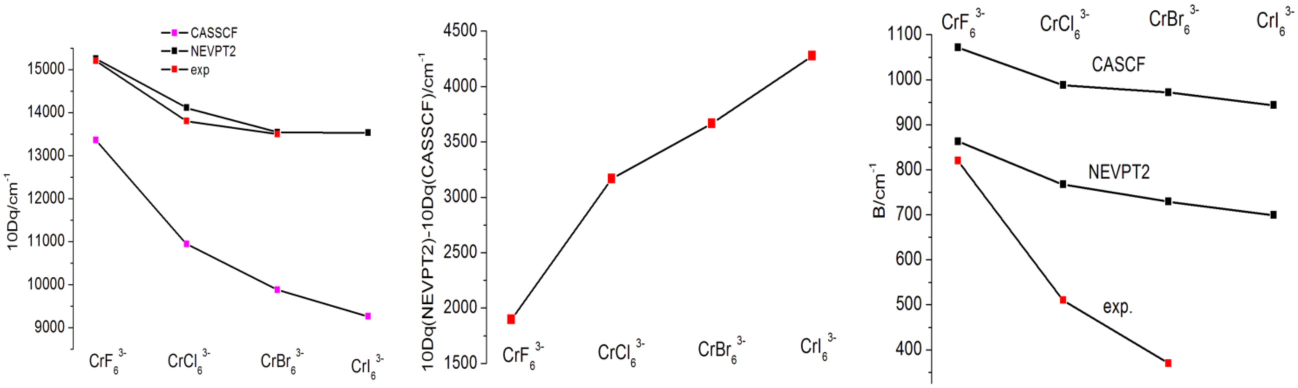


Figure 4. Ligand field parameters 10Dq (left) and B(right) from analysis of CASSCF/NEVPT2 *ab initio* wavefunction in comparison with data extracted from a direct fit to reported spectra (exp. C.K.Jørgensen, Absorption spectra and Chemical Bonding in Complexes, Pergamon, 1962, p. 110, Oxford); variation of metal ligand covalence along the series has been approximated as the difference between 10Dq(NEVPT2) (dynamical correlation accounted for), and 10Dq(CASSCF), (CAS(3,5) active space, dynamical correlation neglected) amidst.

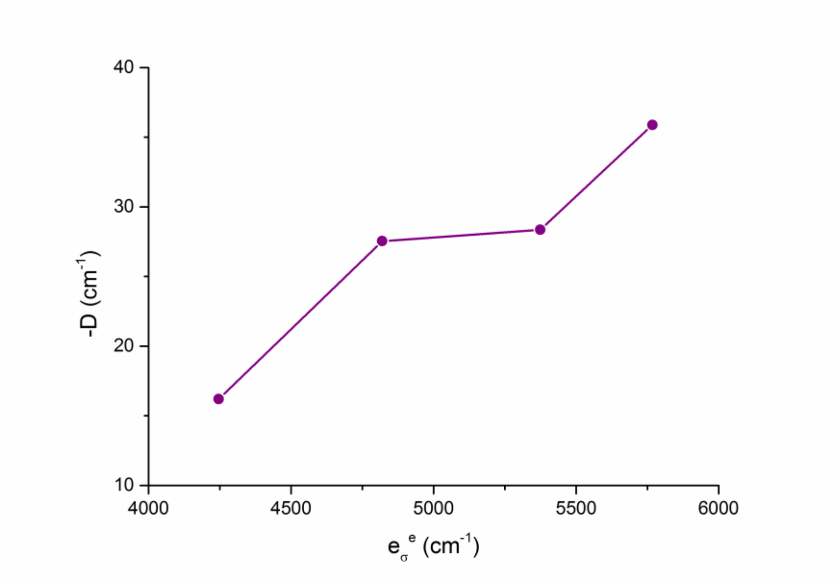


Figure 5. Relation between the e_s^e AOM parameter and the axial zero field splitting parameter D. The e_s^e parameter value can be interpreted as proportional to the σ-donor ability of the corresponding derivative of the trianionic tris(pyrrolyl-α-methyl) amines tpa^R (from left to right:R=tBu=*tert*-butyl, Mes=mesityl, Ph=phenyl and DFP=2,6-difluorophenyl) ligand for the complexes depicted in Figure 1.

Magneto-Structural Correlations in Pseudo-tetrahedral Co^{II} Complexes[13].

Cobalt(II) tetra-thiolate $[Co(SPh)_4]^{2-}$ was reported as a *first example of a mononuclear SMM that shows a slow relaxation of the magnetization in the absence of an external magnetic field*. [11] Substitution of the donor ligand atom by oxygen or selenium dramatically changes ZFS and relaxation time. The series of complexes $(PPh_4)_2[Co(XPh)_4]$ (X=O, S, Se) [12] have been studied *using multi-reference ab initio methods with the goal of exploring the effect of the tetragonal elongation* $T_d \rightarrow D_{2d}$, *described the angle* $2\theta<109.47^o$, *and the torsion angle* ψ *describing the change of symmetry from* $D_{2d}(\psi=0^o$, *all-vertical configuration) toward various degrees of* S_4 *distortions* ($\psi=90^{o}$, *ultimately all-horizontal configuration), the latter being imposed by the second coordination sphere, the C atoms directly connected to X Fig. 2). Magnetostructural correlations are then deduced that take into account the nature of metal-ligand covalent bonding, ligand spin-orbit coupling and the geometric distortions just described.* The absolute value of zero-filed splitting D increases when the ligand field strength decreases across the series from O to Te. The zero-field splitting (ZFS) of the ground state of the hypothetical $[Co(TePh)_4]^{2-}$ complex has been computed to be about twice as large as for the well-known $(PPh_4)_2[Co(SPh)_4]$ compound. It is shown that magneto-structural correlations in $[Co(OPh)_4]^{2-}$ type complexes differ from $[Co(S/SePh)_4]^{2-}$ due to the π-anisotropy of the ligand donor atoms (S, Se). In the case of almost isotropic OPh ligand only variations in the first coordination sphere affect magnetic properties, but in the case of S/SePh ligand variations in the first and second coordination sphere become equally important for the magnetic properties.

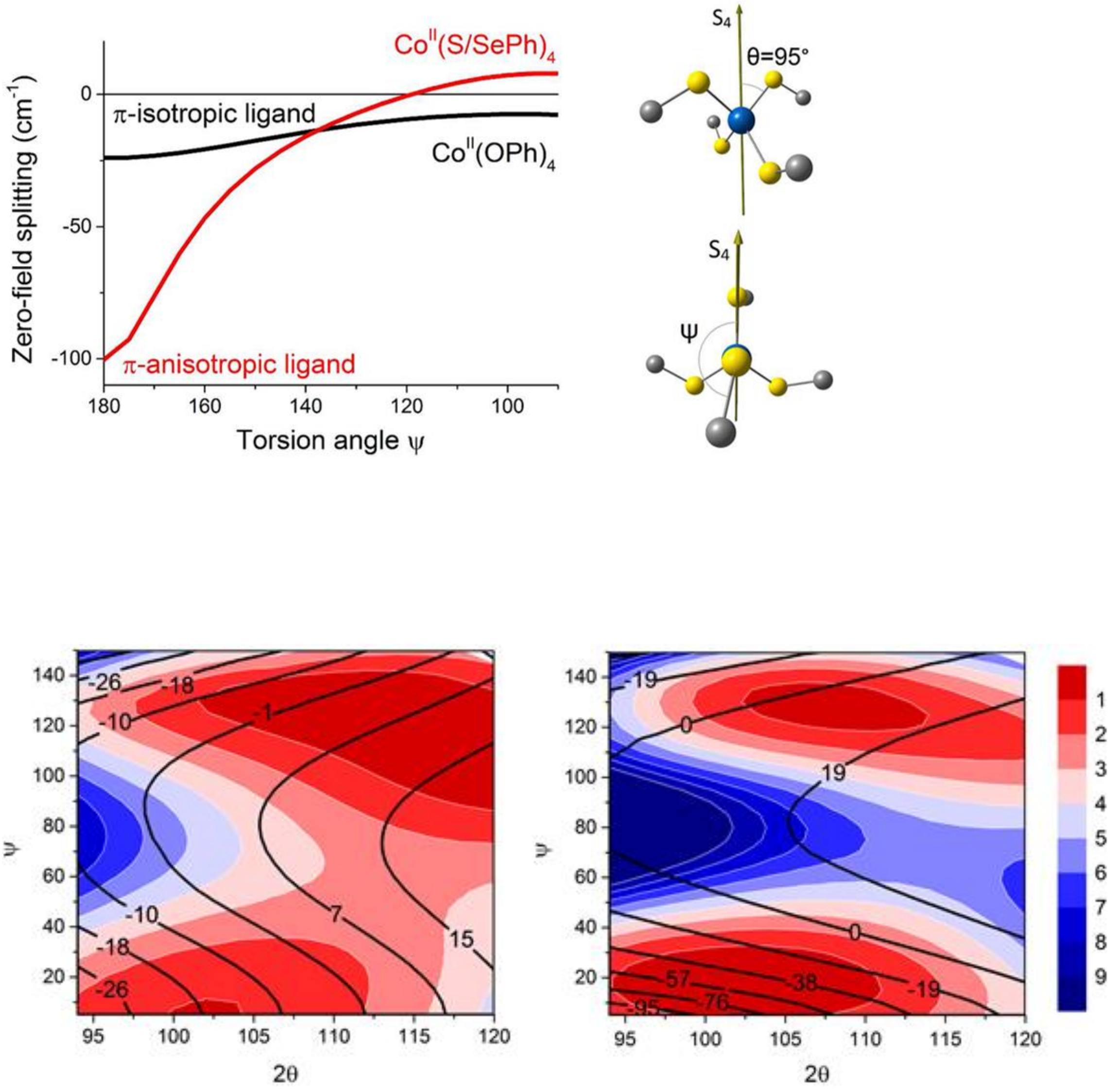


Figure 6. The first and the second coordination sphere of Co ion along with the two angles θ and ψ defining the lowering of symmetry from T_d to D_{2d} and S_4(top, right); interplay between Co-X π-antibonding and ψ and their effect on D (top left) and two-dimensional relaxed surface scan (shown in colors according to color code on the right in kcal/mol) and the corresponding values of the zero-filed splitting (black contour lines in cm^{-1}) of the $[Co(OMe)_4]^{2-}$ (left)and $[Co(SeMe)_4]^{-2}$ (right) complexes (adopted from Ref. 13).

Along the same lines we have analyzed the electronic structure of a new magnetically bi stable mononuclear tetragonally elongated tetrahedral cobalt(II) complex $(HNEt_3)_2[Co^{II}(L^{2-})_2]$ with nitrogen donors (Fig. 7).[14] The two very acute axial NCoN chelate angles along with the strong ligand field induce a large t_2 splitting and leads to a lowest $^4B_2$ excited states which is only 500 cm^{-1} above the ground state and thus comparable with spin-orbit coupling parameter ζ. The large mixing of these states via spin-orbit coupling leads to easy axis anisotropy and an unusually large D parameter (-115 cm^{-1}). It explains the observed magnetic bi stability manifesting in an open hysteresis loop (coercitivity) in the magnetization at a sweep rate dB/dt=3.0T/min.[14]

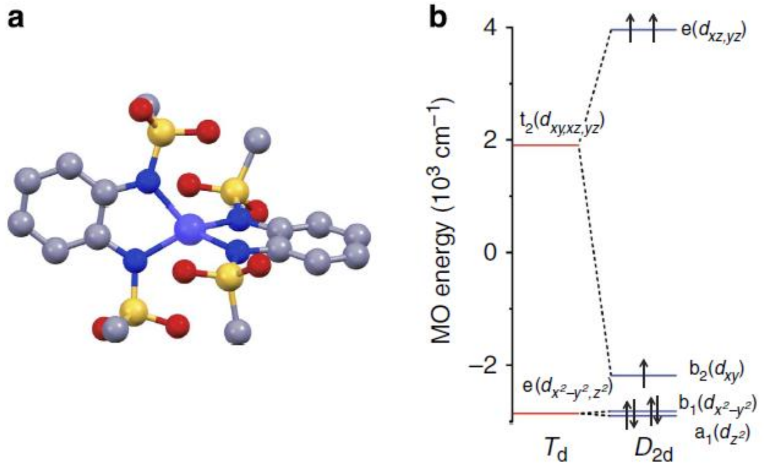


Figure 7. Molecular and electronic structure of the complex [Co^{II}(L^{2-})$_2$]: a)Crystallographic structure, Cobalt, Oxygen, Sulfur, Nitrogen and Carbon are shown in blue, red, yellow, violet and grey, respectively, Hydrogen atoms are omitted for clarity. b) Molecular obital diagram from CASSCF/NEVPT2 AILFT analysis of CAS(7,5) wave functions; horizontal lines depict orbital energies while arrows pointing up or down stand for single electron spins; the given configuration pertains to the $^4B_1$ ground state which mixes with the lowest excited $^4B_2$ state via the L_zS_z part of the spin-orbit coupling operator (adopted from Ref.14).

From these studies design principles toward novel SMM with improved magnetic anisotropies emerge as follows: magnetic bi stability in tetrahedral Co(II) complexes is enforced by:

i) Soft ligands inducing week ligand fields along with a tetragonally elongated complex (D_{2d}) geometry.

ii) Chelate ligands with strong donor ligands (such as N) imposing very acute NCoN trans chelate angles that afford large D_{2d} $^4B_2$<^4E splitting of the $^4T_2$ excited state and, via SOC mixing of $^4B_2$ with the ground state $^4B_1$ highly anisotropic magnetic moments.

III.Complexes of lanthanides [15].

Periodic trends on structural and spectroscopic properties of complexes of lanthanides have been examined through complete active space self-consistent field (CASSCF) followed by second order N-electron valence perturbation theory (NEVPT2) calculations including both scalar relativistic and spin-orbit coupling effects [Fig.8]. Energies and wave functions from electronic structure calculations are further analyzed in terms of *ab initio* Ligand Field theory (AILFT), which allows one to rigorously extract angular overlap model (AOM) ligand field, Racah and spin orbit coupling parameters directly from high-level *ab initio* calculations. We investigated the elpasolite $Cs_2NaLn^{III}Cl_6$ (Ln^{III}=Ce-Nd, Sm-Eu, Tb-Yb) crystals because these compounds have been synthesized for most Ln^{III} ions. $Cs_2NaLn^{III}Cl_6$ elpasolites have been also thoroughly characterized with respect to their spectroscopic properties, providing an exceptionally vast and systematic experimental database allowing one to analyze the periodic trends across the lanthanide series. Particular attention has been devoted to the apparent discrepancy in metal-ligand covalency trends between theory and spectroscopy described in the literature. Consistent with earlier studies, natural population analysis indicates an increase in covalency along the series, while a decrease in both the nephelauxetic (Racah) and relativistic nephelauxetic (Spin-orbit coupling) reduction with increasing atomic number is calculated. These apparently conflicting results are discussed on the basis of AILFT parameters. The AILFT derived parameters faithfully reproduce the underlying multireference electronic structure calculations. The remaining discrepancies with respect to experimentally derived data are mostly due to underestimation of the ligand field splittings, while the dynamic correlation and nephelauxetic effects appears to be adequately covered by CASSCF/NEVPT2.

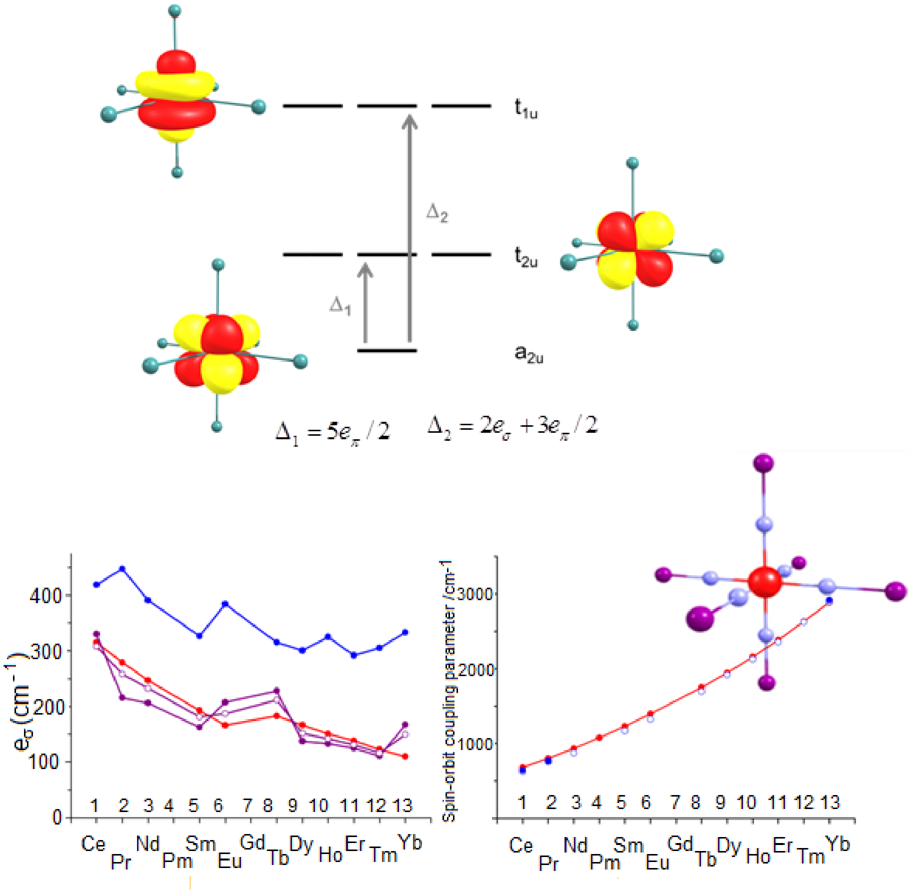


Figure 8. Splitting of f-orbitals in octahedral ligand field (top); Experimental (blue) and calculated (CASSCF:red, NEVPT2: purple) e_σ parameters for LnCl$_6$(bottom left); e_π (not shown) displays a similar trend; ab initio spin-orbit coupling parameter ζ for lanthanide ions: available experimental data from free ions (blue filled circles) and for the Cs$_2$NaLn^{III}Cl$_6$ series (blue open circles), bottom right; the electron occupation of the f-shell is shown above the abscissa.

Project key publications:

[1] What is not required to make a single molecule magnet. Neese, F., Pantazis D.A., Faraday Discussions, 148(2011) 229-238.

[2] Slow Magnetic Relaxation in a High-Spin Iron(II) Complex, Freedman, D. E.; Harman, W. H.; Harris, T. D.; Long, G. J.; Chang, C. J.; Long, J. R., *J. Am. Chem. Soc.* 2010, *132*, 1224-1225.

[3] Slow Magnetic Relaxation in a Family of Trigonal Pyramidal Iron(II) Pyrrolide Complexes, Harman, W. H.; Harris, T. D.; Freedman, D. E.; Fong, H.; Chang, A.; Rinehart, J. D.; Ozarowski, A.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Long, J. R.; Chang, C. J. *J. Am. Chem. Soc*., 2010, *132*, 18115-18126.

[4] A Detailed *Ab Initio* First-Principles Study of the Magnetic Anisotropy in a Family of Trigonal Pyramidal Iron(II) Pyrrolide Complexes, Atanasov,M.; Ganyushin, D.; Pantazis, D.A. Sivalingam, K.; Neese, F. Inorg.Chem. 2011, 50, 7460-7477.

[5] Slow magnetization dynamics in a series of two-coordinate iron(II) complexes, Zadrozny, J.M.; Atanasov M., Bryan,A.M.; Lin,C.; Rekken,B.D.; Power,P.P; Neese, F.; Long, J.R.; Chem.Sci., 2013, 4, 125-138.

[6] A theoretical analysis of chemical bonding, vibronic coupling, and magnetic anisotropy in linear iron(II) complexes with single-molecule magnet behavior, Atanasov,M.; Zadrozny,J.M.; Long,J.R; Neese, F.; Chem.Sci., 2013, 4, 139-154.

[7] Magnetic blocking in a linear iron(I) complex, Zadrozny, J.M.; Xiao, D.J.; Atanasov, M.; Long, G.J.; Granjean, F.; Neese, F.; Long, J.R. Nature Chemistry, 2013, 5, 577-581.

[8] Vibronic Interactions and the Jahn-Teller Effect, Theory and Applications, M.Atanasov, C.Daul, P.L.W.Tregenna-Piggott (eds), Springer, 2012.

[9] A.Modern First-Principles, View on Ligand Field Theory Through the Eyes of Correlated Multireference Wavefunctions, Atanasov, M.; Ganyushin, D.; Sivalingam, K.; Neese, F., in:Mingos, D.M.P.; Day, P.; Dahl, J.P. (Eds.); Struct.Bonding, 2012, 143, 149- 220.

[10] First Principles Approach to the Electronic Structure, Magnetic Anisotropy and Spin Relaxation in Mononuclear 3d-Transition Metal Single Molecule Magnets, Atanasov, M.; Aravena,D.; Suturina, E.; Bill, E.; Maganas, D.; Neese, F.; Coord.Chem.Rev. 289-290(2015), 177-214.

[11] Zadrozny, J. M.; Long, J. R. J Am Chem Soc 2011, 133, 20732.

[12] Zadrozny, J. M.; Telser, J.; Long, J. R. Polyhedron 2013, 64, 209.

[13] Suturina, E.A., Maganas,D., Bill,E., Atanasov,M., Neese, F., Magneto-Structural Correlations in a Series of Pseudotetrahedral [CoII(XR)4]2− Single Molecule Magnets: An ab Initio Ligand Field Study, Inorg.Chem., 2015, 54, 9948-9961

[14] Rechkemmer,Y., Breitgoff, F.D., van der Meer,M., Atanasov,M., Hakl,M., Orlita, M.,Neugebauer,P., Neese, F., Sarkar, B.,van Slageren, J., A four-coordinate cobalt(II) single-ion magnet with coercivity and a very high-energy barrier, *Nature Communications,* 2016, 7:10467 | DOI: 10.1038/ncomms10467.

[15] Aravena, D.; Atanasov,M.,Neese, F. Periodic Trends in Lanthanide Compounds through the Eyes of Multireference ab Initio Theory, *Inorg.Chem.*2016,55,4457-4469.

(Forschungsbericht Prof. Dr. Mihail Atanasov, Stand: Januar 2018)