

# CHAPTER 4

---

## REGULAR APPROXIMATION APPROACH FOR PREDICTION OF MAGNETIC PARAMETERS IN Co(II) COMPLEXES AND THEIR CORRELATION WITH CHEMICAL REACTIVITY

### INTRODUCTION

While studying the enhanced properties pertaining to the single molecule magnets, it has become obvious that the magnetic anisotropy is the main criterion for exhibiting slow relaxation of the magnetization. Relaxation of the magnetization is a characteristic which in turn is affected by the ligand-field, molecular symmetry and single-ion effects of spin-orbit coupling and zero-field splitting [1]. The slow magnetic relaxation behaviour was first observed when Co(II) single molecule magnets (SMMs) were reported in 2002 [2]. These types of investigations focused on increasing the total spin of the molecular ground state. This is so because the properties of the SMMs are associated with an energy barrier for the reversal of the molecular magnetic moment [3].

This work presents a detailed evaluation of the performance of DFT for the prediction of zero-field splitting in tetra-coordinate cobalt complexes  $[\text{CoCl}_2\text{L}_2]$ . Among first row transition metal complexes highest attention is being paid to Co(II) complexes due to their formation of various forms of coordination polyhedral and large magnetic anisotropy. A variety of single ion molecules (SIMs) of Co(II) were reported in the form of tetrahedral or pseudotetrahedral coordination [4–7]. Only a few are reported in the geometry of square-pyramidal [8–10], trigonal bipyramidal [11], octahedral [12,13] and trigonal prismatic form [14,15]. Winfried Plass *et. al.* reported a distorted tetrahedral Co(II) complex with two bidentate 2-(<sup>1</sup>H-imidazol-2-yl)phenol-based ligands and it was the first Co(II) complex exhibiting single molecular magnetic behaviour with N, O donor environment [16]. Theoretically calculated magnetochemical [17] parameters like g-tensors, D-tensors etc. can open the perspective of establishing a magnetostructural correlation for magnetic anisotropy that would allow chemists to tune and eventually control various magnetic parameters in transition metal complexes.

Here we have studied a series of mononuclear Co(II) complexes with L being heterocyclic N donor. The complexes are namely,  $[\text{CoCl}_2(\text{NH}_2\text{pymd})_2]$  (**1**),

[CoCl<sub>2</sub>(bziz)<sub>2</sub>] (2), [CoCl<sub>2</sub>(dmpz)<sub>2</sub>] (3) and [CoCl<sub>2</sub>(NO<sub>2</sub>dmiz)<sub>2</sub>] (4) where the abbreviations for the ligands stand for: dmpz= 3,5-dimethylpyrazole, NO<sub>2</sub>dmiz= nitro-N-dimethylimidazole, NH<sub>2</sub>pymd= 2-aminopyrimidine and bziz=benzimidazole. This set of Co(II) complexes are experimentally studied by Idešicová, M., *et al.* [17].

#### 4.1 Theory

Cobalt complexes with tetrahedral symmetry with a <sup>4</sup>A<sub>2</sub> ground term with two Kramers doublet may have both positive and negative zero-field splitting D-tensor values and exhibit single molecular magnetic properties. The determination of D-tensor is vital because it for Kramers systems, the D-tensor is required in the formula for barrier to spin reversal

$$U_{eff} = |D| \left( S^2 - \frac{1}{4} \right)$$

The orbitally degenerate ground terms in tetracoordinate Co(II) complexes are <sup>4</sup>A<sub>2</sub> in T<sub>d</sub> symmetry, <sup>4</sup>B<sub>1</sub> in D<sub>2d</sub> symmetry, <sup>4</sup>A<sub>2</sub> in C<sub>v</sub>, <sup>4</sup>A<sub>1</sub> in C<sub>s</sub> and <sup>4</sup>A in C<sub>1</sub> symmetry these ground terms split into ground and excited multiplets to Kramers doublet |S, M<sub>S</sub>⟩ and they are separated by

$$2D = E \left( \left| \frac{3}{2}, \pm \frac{3}{2} \right| \right) - E \left( \left| \frac{3}{2}, \pm \frac{1}{2} \right| \right)$$

The g-tensor can be considered as a second-order property of EPR [18,19]. The decomposed form of electronic g-tensor is:

$$\mathbf{g} = \mathbf{g}_e \mathbf{1} + \Delta \mathbf{g}$$

where ‘ $\mathbf{g}$ ’ stands for electronic g-tensor,  $\mathbf{g}_e$  is the g-factor for free electron (2.0023) and  $\Delta \mathbf{g}$  is the g-tensor shift. The g-shift is unique to every molecule since it is a characteristic quantity of the local environment of the unpaired electrons in the molecule. The detailed theory of D-tensor or zero-field splitting is discussed in the earlier chapters.

## 4.2 Computational Details

In this present work we have used ECP(SDD) basis set for Co(II) ion while def2-TZVP/J for the remaining atoms which includes Cl, N, O etc. The functional that we have opted for is BP [20,21]. For geometry optimizations we have used *TightSCF* instead of *NormalSCF* in order to reduce noise in the gradients. For convergence of SCF we have opted for slow convergence using *SlowConv* feature. While calculating the magnetic parameters we have taken UKS module which stands for unrestricted Kohn-Sham reference wave functions and RI (Resolution Identity) approximation is used in the SCF part. The accurate spin-orbit mean-field method (SOMF) developed by Hess, Marian, Wahlgren, and Gropen [22] is put into the input which defines the details of the spin-orbit coupling operator. The mean-field method is taken into consideration in order to achieve a realistic computation of zero-field splitting in the concerned complexes. This is acceptable if the second-order spin-orbit coupling contributions are not remarkably large which is true in most of the cases.  $D_{SOC}$  part is calculated using the Coupled Perturbed (CP) method which is a generalization of the DFT for ZFSs. It uses revised pre-factors for the spin-flip terms and solves a set of coupled-perturbed equation for the SOC perturbation. On the other hand,  $D_{ss}$  term being an expectation value uses the spin-density of the system.

The output gives information about the g tensor (relativistic mass correction  $\Delta g_{RMC}$ , diamagnetic spin-orbit term  $\Delta g_{GC}$ , paramagnetic spin-orbit term (OZ/SOC)  $\Delta g_{SO/OZ}$ , the isotropic g value  $g_{iso}$  and the orientation of the total D-tensor. It also computes the contributions from spin-orbit coupling and spin-spin term towards D-tensor.

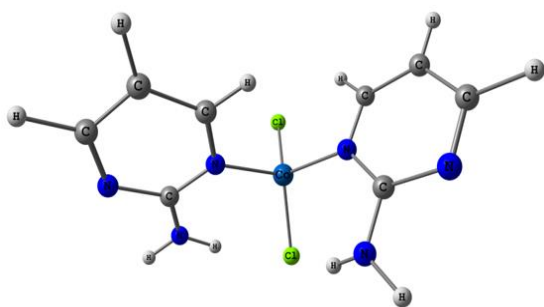
Geometry optimization has been done by using ORCA program package [23]. The basis sets used for geometry optimization are ECP(SDD) [24,25] for Co(II) ions and def2-TZVP/J for the remaining atoms which include Cl, O, N, etc. we have used BP functional. Earlier studies by other studies have revealed that the Coupled-Perturbed method (CP) is more efficient in calculating D-tensors and g-tensors in transition metal complexes [26]. Hence in this study also we have used the CP method.

Also a comparative study between ZORA and relativistic IORA approach is being made [27–29] ZORA is zero-order regular approximation while IORA stands for infinite-order regular approximation. The term IORA was coined by Dyllal and van Lenthe [30] in 1999. In ORCA the spin-free variant is implemented which makes IORA a suitable starting point for the development of second order regular approximation. The core levels of heavy elements are not appropriately reproduced in ZORA. Also in case of IORA, which is being of higher order regular approximation appreciably improves the situation by approaching the Dirac eigenvalues much better than the ZORA method. Hence it is seen that the ZORA equation with a modified metric operator yield the IORA form. Therefore, we have discarded the results from ZORA and only considered the IORA readings of the magnetic properties. Mathematically, the equation for IORA above is

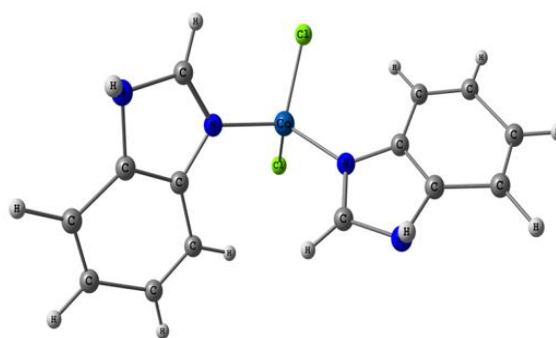
$$\hat{H}^{IORA} \Psi^{IORA} = E^{IORA} \Psi^{IORA}$$

Though IORA has poor gauge invariance, it is corrected by NESC (normalized elimination of small components).

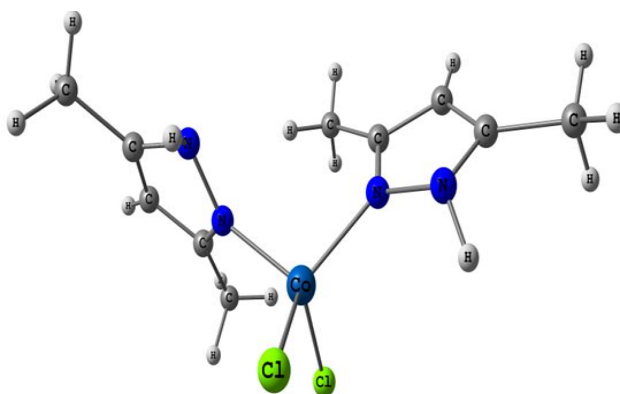
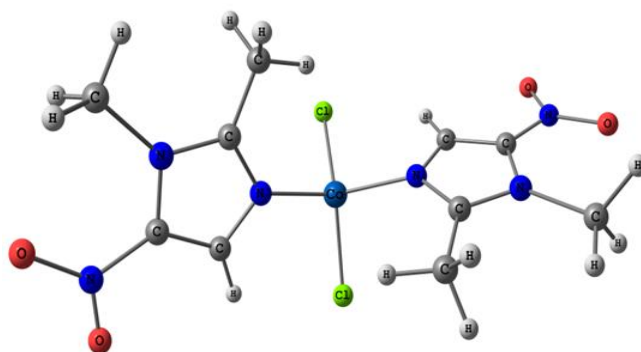
### 4.3 Results and discussion



(1)  $[\text{CoCl}_2(\text{NH}_2\text{pymd})_2]$



(2)  $[\text{CoCl}_2(\text{bziz})_2]$

(3) [CoCl<sub>2</sub>(dmpz)<sub>2</sub>](4) [CoCl<sub>2</sub>(NO<sub>2</sub>dmiz)<sub>2</sub>]**Figure 4.1:** Optimized structures of Co[Cl<sub>2</sub>L<sub>2</sub>] complexes

### 4.3.1 Calculation of g-tensors in the Co[Cl<sub>2</sub>L<sub>2</sub>] complexes

We have performed single point calculations of magnetic properties, viz. D-tensor and g-tensor on the optimized geometries of these Co(II) complexes. The experimental and the theoretical values obtained by this work are being compared. Due to spin-orbit coupling of the metal in ionic state the free electron g-tensor deviates from  $g_e=2.0023$ . Table 4.1 shows the calculated g-tensors in x, y and z axes and also the  $\Delta g_{iso}$  values.

**Table 4.1:** Calculated g-tensors of Co(II) complexes

Sl. No.	Complex	$g_x$	$g_y$	$g_z$	$g_{iso}$	$\Delta g_{iso}$
(1)	[CoCl <sub>2</sub> (NH <sub>2</sub> -pymd) <sub>2</sub> ]	2.286	2.198	2.117	2.200	0.198
(2)	[CoCl <sub>2</sub> (bziz) <sub>2</sub> ]	2.296	2.214	2.261	2.257	0.255
(3)	[CoCl <sub>2</sub> (dmpz) <sub>2</sub> ]	2.546	2.460	2.068	2.358	0.356
(4)	[CoCl <sub>2</sub> (NO <sub>2</sub> dmiz) <sub>2</sub> ]	2.064	2.109	2.136	2.103	0.101

We have obtained g-values close to 2 which implies anisotropy of Zeeman interaction being very small. The isotropic g-tensors show deviation from the free-electron g-value and as mentioned above this deviation is attributed to the spin-orbit interaction of Co(II) ion with the ligand field environment. Such spin-orbit interaction is absent in case of free Co atom. Since different ligands enforce different ligand field effect hence the magnetic environment around the different ligands varies and this further causes divergence in the free g-tensor value, i.e.  $g_e=2.0023$ . The g-shifts are dominated by the  $\Delta g_{iso}$  contributions which is the average g-value in all the three axes. We have also calculated the various contributing terms towards g-tensor which include the spin-orbit/orbital Zeeman term ( $\Delta g_{SO/OZ}$ ), the relativistic mass-correction term ( $\Delta g_{RMC}$ ) and the gauge-correction term ( $\Delta g_{GC}$ ) and this is tabulated below in Table 4.2.

**Table 4.2:** Decomposition of g-tensor values

Sl. No.	Complex	$\Delta g_{RMC}$	$\Delta g_{SO/OZ}$	$\Delta g_{GC}$
(1)	[CoCl <sub>2</sub> (NH <sub>2</sub> -pymd) <sub>2</sub> ]	2.001	0.00036	0.099
(2)	[CoCl <sub>2</sub> (bziz) <sub>2</sub> ]	2.001	0.00038	0.122
(3)	[CoCl <sub>2</sub> (dmpz) <sub>2</sub> ]	2.001	0.00035	0.056
(4)	[CoCl <sub>2</sub> (NO <sub>2</sub> dmiz) <sub>2</sub> ]	2.001	0.00037	0.101

From this table it is evident that there is no uniform pattern for contribution from these terms towards the total g-tensor, i.e., no particular percentage of contribution comes from any of these terms. Hence we can not draw any conclusion as from which term contribution is the most or so or which term would dominate the total g-tensor. In Table 4.3 we have compared between the experimental g-values and our calculated g-tensors.

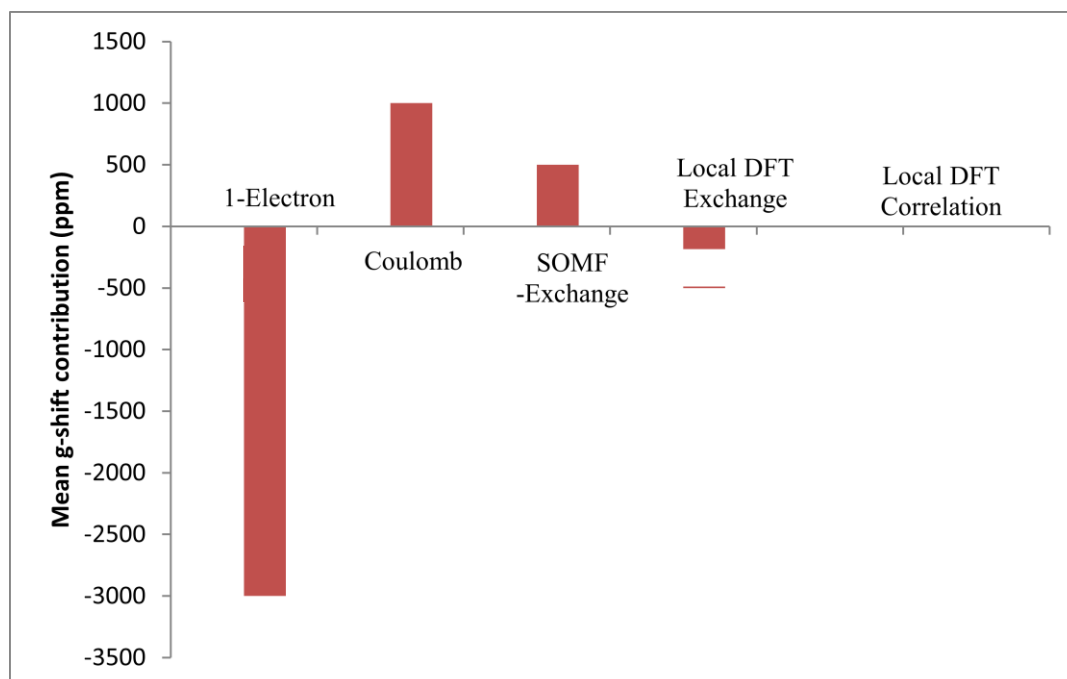
**Table 4.3:** Comparison between experimental and theoretical g-tensors

Sl. No.	Complexes	$g_{iso}$ (experimental)	$g_{iso}$ (theoretical)
(1)	[CoCl <sub>2</sub> (NH <sub>2</sub> -pymd) <sub>2</sub> ]	2.161	2.200
(2)	[CoCl <sub>2</sub> (bziz) <sub>2</sub> ]	2.290	2.257
(3)	[CoCl <sub>2</sub> (dmpz) <sub>2</sub> ]	2.000	2.358
(4)	[CoCl <sub>2</sub> (NO <sub>2</sub> dmiz) <sub>2</sub> ]	2.163	2.103

The g-tensor values are close to 2 and this reveals that the anisotropy of the Zeeman interaction are very small. Since different ligands enforce different ligand field effect hence the magnetic environment around the different ligands varies and this further causes divergence in the free g-tensor value, i.e.  $g_e=2.0023$ . The comparison between the experimental and the theoretical result shows that the IORA approach compensates for the drawbacks which are otherwise faced in case of the ZORA calculations. Combinations of the coupled-perturbed method (CP) as well as the relativistic approach IORA shows g-tensor values close to the experimentally obtained results.

We have also computed the individual contributions of g-tensor terms to the spin-orbit operator or the SOC operator. The g-shifts from each of the terms are either positive or negative, hence we have taken the mean of sum of the absolute values for each contribution for the four complexes. But we have assigned relative signs to each contribution





**Figure 4.2:** Individual contributions of g-tensor terms to the SOC operator

The highest contribution to the SOC operator is from the one-electron term. The second highest contribution is from the two-electron Coulomb term but being of opposite sign it cancels approximately 30% on average of the one-electron term. The local DFT exchange contributes almost 14% of the one-electron term. This enhances the shielding exerted by the Coulomb term. Local DFT correlation is very inconsequential and amounts to  $\sim 0.05\%$  of the one-electron contribution.

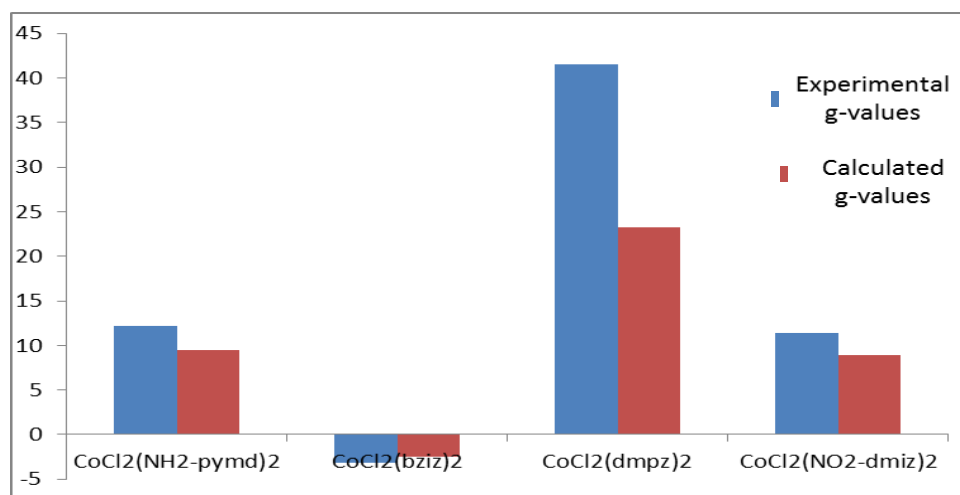
### 4.3.2 Calculation of D-tensors in the $\text{Co}[\text{Cl}_2\text{L}_2]$ complexes

After the g-tensor values were obtained we have calculated the D-tensors for these four Co(II) complexes and compared with the experimental values from the references cited. We have performed D-tensor calculation using the coupled perturbed (CP) method which one of the best form of DFT calculation for EPR parameters. Once we have obtained the coupled perturbed orbitals we opted for ROCIS method which has given values very close to the experimental values. In most of the studies coupled perturbed (CP) method for spin-orbit interaction has proved to give results closer to the experimental D-values. We have calculated the correlation for the theoretical and the experimental D-tensor

values which has come to be 0.98. Table 4.4 shows the comparison between the experimental and theoretical D values.

**Table 4.4:** Comparison between experimental and theoretical D-tensors

Sl. No.	Complex	D(in $\text{cm}^{-1}$ ) experimental	D(in $\text{cm}^{-1}$ ) theoretical
(1)	$[\text{CoCl}_2(\text{NH}_2\text{-pymd})_2]$	12.20	11.378
(2)	$[\text{CoCl}_2(\text{bziz})_2]$	-3.15	-2.697
(3)	$[\text{CoCl}_2(\text{dmpz})_2]$	41.50	39.105
(4)	$[\text{CoCl}_2(\text{NO}_2\text{dmiz})_2]$	11.40	10.267



**Figure 4.3:** Comparison between experimental and theoretical D-tensors

The positive or negative D-tensor is a resultant of the lowest crystal-field multiplet.  $\Delta = 2D > 0$  is proved to be true when the Kramers doublet  $M_S = \pm \frac{1}{2}$  represents ground state and  $M_S = \pm \frac{3}{2}$  is the excited state. We can say that in complex (2)  $[\text{CoCl}_2(\text{bziz})_2]$  is slightly elongated with  $D < 0$  while the same part in the other three complexes is slightly compressed and  $D > 0$ . Also the large positive D-tensor values in these complexes except  $[\text{CoCl}_2(\text{bziz})_2]$  is attributed to the slow relaxation of magnetization. This large magnitude

of positive D-values is said to arise due to spin-orbit coupling originating from mixing of the ground state with two excited electronic levels. The positive or negative sign of D-tensor is also consistent with the g-factor asymmetry. Complex (2) has greater deviation from free electron g-tensor value and reported to have D-tensor with negative sign.

The combined IORA and the coupled perturbed method (CP) gave theoretical D-tensors quite close to the experimental D-tensor values. IORA when paired with the NESC gives results quite close to the established values. Therefore, in future studies we can use this combination of approaches in order to predict the sign of D-tensors which in turn would predict whether a given transition metal complex is able to exhibit characteristics of single-molecule magnet (SMM) or not. However, it should be considered that when IORA not paired with NESC give poor results as the variable for relativistic approach is not reproduced.

The Co atoms gain partial positive charges while the N or O atoms bound to them possess partial negative charges. This assures significant separation of charges between Co and N or O atoms and shows the Co–N and Co–O bonding to be covalent. It can be seen that the bonding between the N-heterocyclic bases and cobalt atom occurs via the anchoring of a Co atom to the N or O atoms of the bases because as a general trend, the Co atom would interact with the more electronegative N or O atoms which possess a lone pair of electron. This suggests a Lewis acid (Co)-base (N or O) type of interaction. There is a structural transition when the ligands connecting via N and O are showing such properties. The bonding is dominated by delocalization of electrons between the Co and O or Co and N atoms.

The Mulliken population and the charge transfer from the metal ion towards the ligands are calculated. The charge densities are distributed from the metal ion towards the more electronegative chloride ligands and it diminishes monotonically towards the nitrogen dentate ligands. The Mulliken analysis reveals that there are about 0.9 to 0.5 electrons transferred from the 4s to 3d orbitals in the Co(II) ions. This shows stronger hybridization in the metal ion and the enforcement of a stronger external magnetic field. Mulliken analysis for these complexes show that there is a valent transition starting due to the electronegativity of the Cl atoms in the complex. It is due to this structural transition that the complexes deviate from the ideal tetrahedral geometry.

### 4.3.3 FMO analysis done on cobalt complexes

Besides magnetic properties of the Co(II) complexes in the present we have also studied the chemical index ‘chemical hardness’ which further leads us to ‘softness’ and we have tried to establish a correlation between magnetic parameters and chemical hardness in case of paramagnetically active complexes. Chemical hardness is a concept of a hard molecule as resisting polarization [31] not being readily deformed in an electric field. In order to define hardness as the curvature of the E vs. N graph we have

$$\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_v = \left( \frac{\partial \mu}{\partial N} \right)_v = - \left( \frac{\partial \chi}{\partial N} \right)_v$$

In this equation  $\mu$  and  $\chi$  are chemical potential and electronegativity of the species respectively. The hardness of the species is then the amount by which its electronegativity decreases when an infinitesimal amount of electronic charge is added to it. Intuitively, a hard molecule is like a rigid container that does not yield as electrons are forced in, so the pressure (analogous to the electron density) inside builds up, resisting the ingress of more electrons. A soft molecule may be likened to a balloon that can expand as it acquires electrons, so that the ability to accept still more electrons is not so seriously compromised. Mathematically softness is the reciprocal of hardness:

$$\sigma = \frac{1}{\eta}$$

and qualitatively, of course, it is the opposite in all ways. The relation of the frontier energy orbitals with chemical hardness is depicted as:

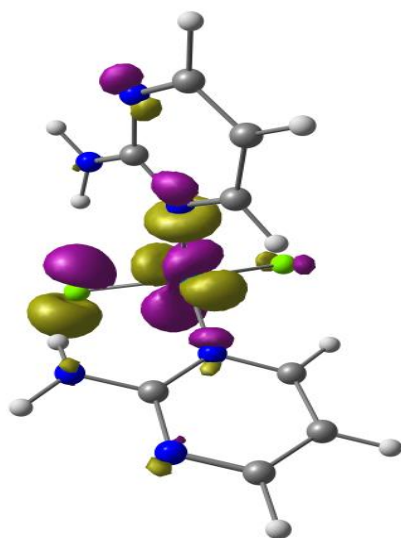
$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2}$$

The stability of a structure can be described by its hardness or softness. The harder the structure or a complex, the more is its stability. Hence the HOMO-LUMO energy of a complex or a cluster is an important tool for the determination of its stability. Substances with larger HOMO-LUMO energy gap are more stable and hence less reactive. Hence we have also calculated the energy gap between the HOMO and LUMO of these complexes by performing the FMO calculations and studied their correlation with the magnetic properties obtained.

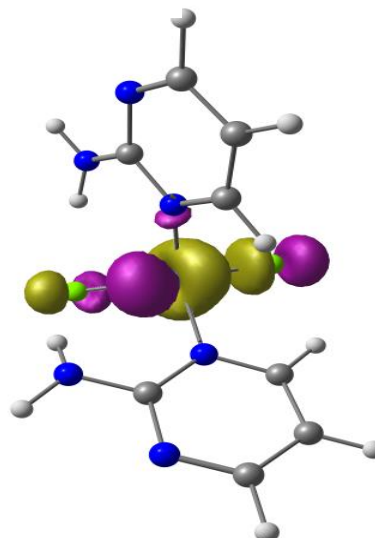
Here the Fixed spin moment approach comes to rescue for establishment of correlation between spin, magnetic moment and HOMO-LUMO gap. This scheme is useful in fixing the total number of electrons between the majority and the minority spin channels. This generates an effective magnetic field in the complexes under study that introduces chemical potential difference between the majority and minority spin electrons. In accordance with the D-tensor values obtained for these systems, when applied to molecular magnets as these complexes, the fixed total moment is obtained in the form of an integer number of Bohr magnetons. It is known that a discrete magnetic molecule has isolated distinct Kohn-Sham energy levels. This leads to a non-zero HOMO-LUMO gap. So in such cases where the HOMO-LUMO gaps overlap, both the majority and minority spin channels possess a common chemical potential. Subsequently an external magnetic field is required to enforce the splitting. In our case, we have considered additional Zeeman term to split the chemical potentials into two spin channels.

From the figures it can be seen that there exists strong intermixing between the electrons of the ligand molecules and the Cobalt atoms. The mixing of orbitals increases due to complexation.

(1) [CoCl<sub>2</sub>(NH<sub>2</sub>-pymd)<sub>2</sub>]

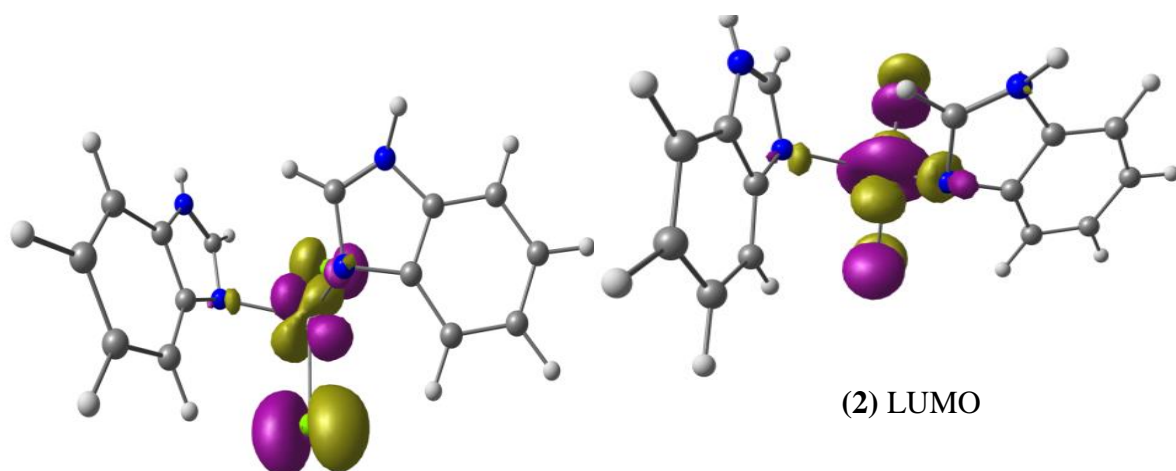


(1) HOMO



(1) LUMO

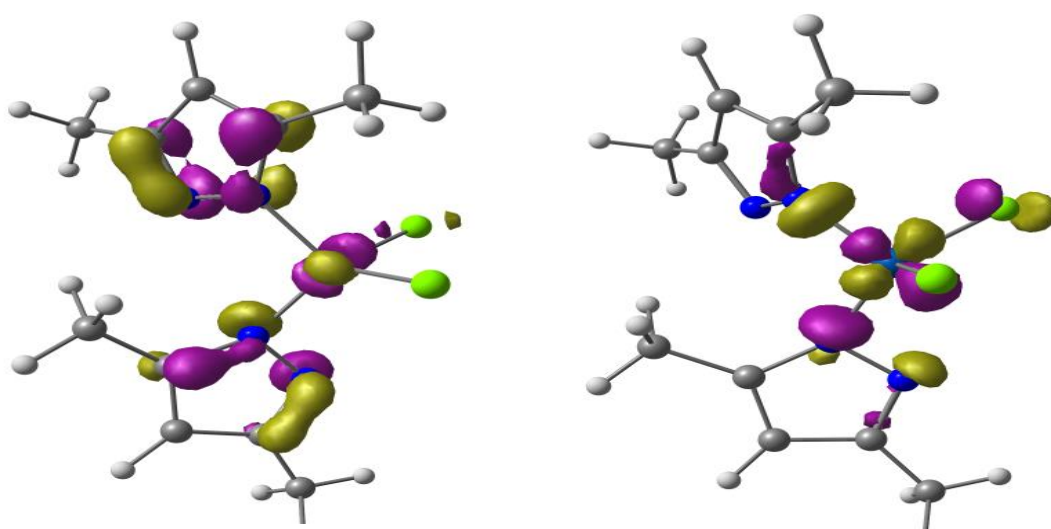
(2)  $[\text{CoCl}_2(\text{bziz})_2]$



(2) HOMO

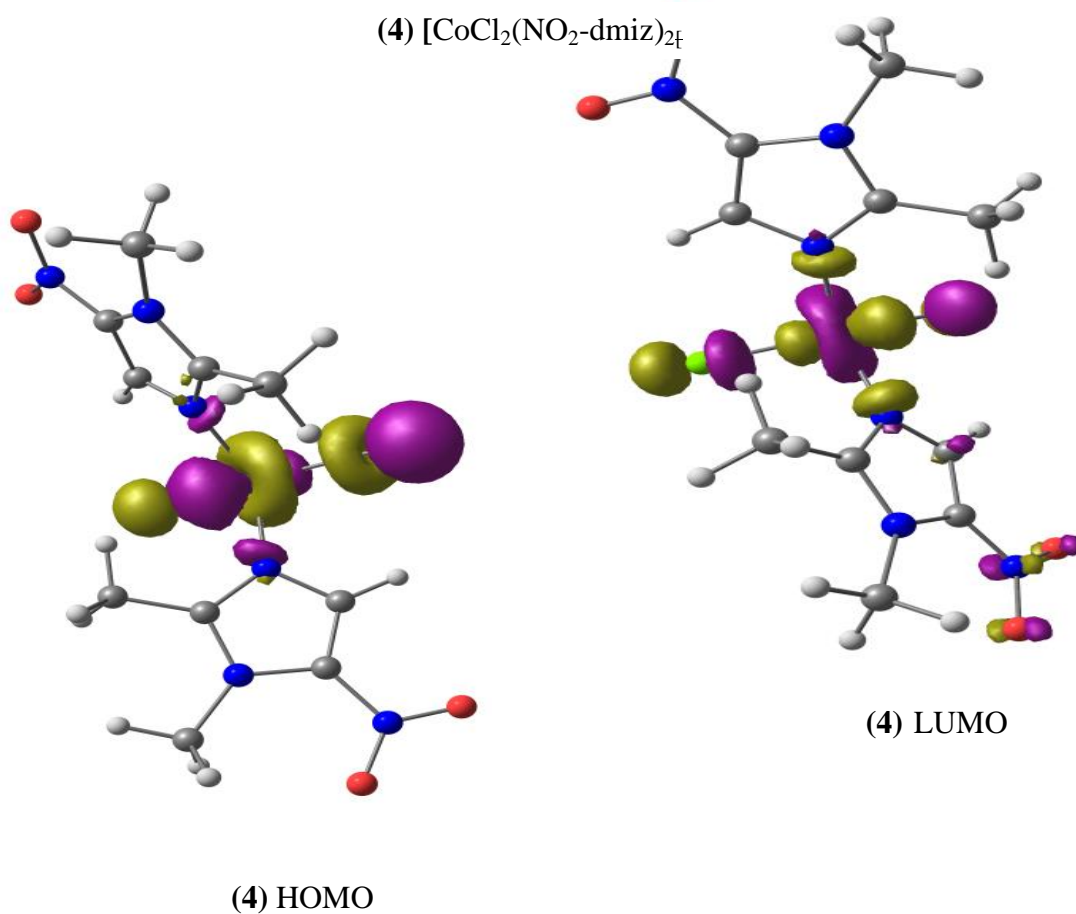
(2) LUMO

(3)  $[\text{CoCl}_2(\text{dmpz})_2]$



(3) HOMO

(3) LUMO



**Figure 4.4:** FMOs of  $\text{Co}[\text{Cl}_2\text{L}_2]$  complexes

$E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  give the chemical hardness ( $\eta$ ) and chemical softness ( $\sigma$ ). Their values are calculated by the following two formulae and shown in Table 4.5:

$$\text{Chemical hardness} = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2}$$

$$\text{Chemical softness} = \frac{1}{\text{Chemical hardness}}$$

**Table 4.5:** Calculated hardness and softness of the complexes

Sl. No.	Complexes	$E_{HOMO}$		$E_{LUMO}$		Hardness	Softness
		(in AU)	(in eV)	(in AU)	(in eV)		
(1)	[CoCl <sub>2</sub> (NH <sub>2</sub> -pymd) <sub>2</sub> ]	-0.199	-5.415	-0.162	-4.408	0.503	1.986
(2)	[CoCl <sub>2</sub> (bziz) <sub>2</sub> ]	-0.22	-5.986	-0.185	-5.034	0.476	2.099
(3)	[CoCl <sub>2</sub> (dmpz) <sub>2</sub> ]	-0.221	-6.013	-0.201	-5.469	0.272	3.674
(4)	[CoCl <sub>2</sub> (NO <sub>2</sub> dmiz) <sub>2</sub> ]	-0.196	-5.333	-0.149	-4.054	0.639	1.563

In terms of chemical hardness, a negative correlation exists for **(4)** [CoCl<sub>2</sub>(NO<sub>2</sub>dmiz)<sub>2</sub>] and **(1)** [CoCl<sub>2</sub>(NH<sub>2</sub>-pymd)<sub>2</sub>] while for other complexes a positive correlation when comparing with the theoretically obtained values. For the experimentally obtained D-tensor values, all complexes show a positive correlation with the corresponding ZFS-parameter. The interpretation of these rather small *D* and *E* values in terms of the detailed coordination environment was found to be challenging since the physical origin of the ZFS tensor is fairly complex, with various contributions resulting from a variety of factors of different physical origins. In this situation quantum chemistry might play an essential role by aiding in the interpretation and rationalization of the observed EPR spectra. This can as well account for determining if a given proposed structure is in accord with the measured D-tensor and elucidating in detail the physical factors that contribute to the observed theoretical ZFS.

Here from the chemical hardness values as **(2)** [CoCl<sub>2</sub>(bziz)<sub>2</sub>] has the smallest value and hence making it highly reactive for its electron cloud over the metal will experience greatest distortion in presence of an electric field. The decrease in the value of D-tensor in the theoretical results is actually due shrinkage of the  $\pi$  system in the ligands. This is caused due to an interaction between the increased spin over the HOMO of benzene ring moiety in each of the ligands and their spin in the LUMO. It is noteworthy that in the [CoCl<sub>2</sub>(dmpz)<sub>2</sub>] complex, the decrease in the D-value from the experimentally obtained value is the highest, almost around 5.7%. It has the least distortion from the ideal



tetrahedral symmetry. This feature is attributed to the more delocalized  $\pi$  cloud over the system as compared to the other three complexes. This is also evident from the FMO diagram of  $[\text{CoCl}_2(\text{dmpz})_2]$ . From the FSM approach the local densities of states (DOS) for the Co(II) ions and the neighbouring ligands it is revealed that for the Co(II) ions in the majority spin channels the local DOS is significantly contributed by an occupied 3d sub-band. On the other hand in the minority spin channel, crystal field splitting is observed that splits into  $t_{2g}$  and  $e_g$  energy levels. The distorted octahedral around the Co(II) ions in these complexes is the reason due to this clear separation.

## REFERENCES

- [1] Ruiz, E., Cirera, J., Cano, J., Alvarez, S., Loose, C. and Kortus, J. Can large magnetic anisotropy and high spin really coexist? *Chemical Communications*, 1:52–54, 2008.
- [2] Yang, E. C., Hendrickson, D. N., Wernsdorfer, W., Nakano, M., Zakharov, L. N., Sommer, R. D. and Christou, G. Cobalt single-molecule magnet. *Journal of Applied Physics*, 91(10):7382–7384, 2002.
- [3] Gatteschi, D. and Sessoli, R. Quantum tunneling of magnetization and related phenomena in molecular materials. *Angewandte Chemie International Edition*, 42(3):268–297, 2003.
- [4] Buchholz, A., Eseola, A. O. and Plass, W. Slow magnetic relaxation in mononuclear tetrahedral cobalt (II) complexes with 2(<sup>1</sup>H-imidazol-2-yl) phenol based ligands. *Comptes Rendus Chimie*, 15(10):929–936, 2012.
- [5] Cao, D. K., Feng, J. Q., Ren, M., Gu, Y. W., Song, Y. and Ward, M. D. A mononuclear cobalt (II)-dithienylethene complex showing slow magnetic relaxation and photochromic behavior. *Chemical Communications*, 49(78):8863–8865, 2013.
- [6] Huang, W., Liu, T., Wu, D., Cheng, J., Ouyang, Z. W. and Duan, C. Field-induced slow relaxation of magnetization in a tetrahedral Co (II) complex with easy plane anisotropy. *Dalton Transactions*, 42(43):15326–15331, 2013.
- [7] Smolko, L., Černák, J., Dušek, M., Miklovič, J., Titiš, J. and Boča, R. Three tetracoordinate Co (II) complexes [Co(biq)X<sub>2</sub>](X= Cl, Br, I) with easy-plane magnetic anisotropy as field-induced single-molecule magnets. *Dalton Transactions*, 44(40):17565–17571, 2015.
- [8] Jurca, T., Farghal, A., Lin, P. H., Korobkov, I., Murugesu, M. and Richeson, D. S. Single-molecule magnet behavior with a single metal center enhanced through peripheral ligand modifications. *Journal of the American Chemical Society*, 133(40):15814–15817, 2011.

- [9] Rajnák, C., Titiš, J., Fuhr, O., Ruben, M. and Boča, R. Single-molecule magnetism in a penta-coordinate cobalt (II) complex supported by an antenna ligand. *Inorganic Chemistry*, 53(16):8200–8202, 2014.
- [10] Habib, F., Luca, O. R., Vieru, V., Shiddiq, M., Korobkov, I., Gorelsky, S. I. and Murugesu, M. Influence of the ligand field on slow magnetization relaxation versus spin crossover in mononuclear cobalt complexes. *Angewandte Chemie International Edition*, 52(43):11290–11293, 2013.
- [11] Ruamps, R., Batchelor, L. J., Guillot, R., Zakhia, G., Barra, A. L., Wernsdorfer, W and Mallah, T. Ising-type magnetic anisotropy and single molecule magnet behaviour in mononuclear trigonal bipyramidal Co (II) complexes. *Chemical Science*, 5(9):3418–3424, 2014.
- [12] Chandrasekhar, V., Dey, A., Mota, A. J. and Colacio, E. Slow magnetic relaxation in Co(III)–Co(II) mixed-valence dinuclear complexes with a  $\text{Co}^{\text{II}}\text{O}_5\text{X}$  (X= Cl, Br, NO<sub>3</sub>) distorted–octahedral coordination sphere. *Inorganic Chemistry*, 52(8):4554–4561, 2013.
- [13] Wu, D., Zhang, X., Huang, P., Huang, W., Ruan, M. and Ouyang, Z. W. Tuning transverse anisotropy in  $\text{Co}^{\text{III}}\text{–Co}^{\text{II}}\text{–Co}^{\text{III}}$  mixed–valence complex toward slow magnetic relaxation. *Inorganic Chemistry*, 52(19):10976–10982, 2013.
- [14] Gomez–Coca, S., Cremades, E., Aliaga–Alcalde, N. and Ruiz, E. Mononuclear single-molecule magnets: tailoring the magnetic anisotropy of first-row transition-metal complexes. *Journal of the American Chemical Society*, 135(18):7010–7018, 2013.
- [15] Zhu, Y. Y., Cui, C., Zhang, Y. Q., Jia, J. H., Guo, X., Gao, C. and Gao, S. Zero-field slow magnetic relaxation from single Co (II) ion: A transition metal single-molecule magnet with high anisotropy barrier. *Chemical Science*, 4(4):1802–1806, 2013.
- [16] Ziegenbalg, S., Hornig, D., Görls, H. and Plass, W. Cobalt (II)-based single-ion magnets with distorted pseudotetrahedral [N<sub>2</sub>O<sub>2</sub>] coordination: Experimental and theoretical investigations. *Inorganic Chemistry*, 55(8):4047–4058, 2016.

- [17] Idešicová, M., Dlháň, L., Moncol, J., Titiš, J. and Boča, R. Zero-field splitting in tetracoordinate Co (II) complexes. *Polyhedron*, 36(1):79–84, 2012.
- [18] Epstein, S. *The Variation Method in Quantum Chemistry*, volume 33, Elsevier, 2012
- [19] McWeeny, R. *Methods of Molecular Quantum Mechanics*. Academic Press, 1992.
- [20] Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A*, 38(6):3098, 1988.
- [21] Perdew, J. P. Erratum: Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Physical Review B*, 34(10):7406, 1986.
- [22] Fernández Rico, J., López, R., Aguado, A., Ema, I. and Ramírez, G. Reference program for molecular calculations with Slater-type orbitals. *Journal of Computational Chemistry*, 19(11):1284–1293, 1998.
- [23] Neese, F., Wennmohs, F., Becker, U., Bykov, D., Ganyushin, D., Hansen, A. and Pantazis, D. A. *ORCA, Version 3.0*. Institute for physical and theoretical chemistry, Bonn, 2014.
- [24] Kahn, O. *Molecular Magnetism*. page 393. VCH Publishers, Inc.(USA), 1993.
- [25] Costa, R., Garcia, A., Ribas, J., Mallah, T., Journaux, Y., Sletten, J. and Rodriguez, V. Tailored magnetic properties in trinuclear copper (II) complexes: Synthesis, structure, and magnetic properties of complexes derived from [1, 3-propanediylbis (oxamato)] cuprate (II)([Cu(pba)]<sup>2-</sup>). *Inorganic Chemistry*, 32(17):3733–3742, 1993.
- [26] Dutta, S. and Deka, R. C. Zero field splitting in Mn (III) complexes: A comparative study of DFT base Coupled–Perturbed and Pederson–Khanna approaches. *Computational and Theoretical Chemistry*, 1072:1–6, 2015.
- [27] Andrae, D., Haeussermann, U., Dolg, M., Stoll, H. and Preuss, H. Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theoretica Chimica Acta*, 77(2):123–141, 1990.

- [28] Dolg, M., Wedig, U., Stoll, H. and Preuss, H. Energy-adjusted ab initio pseudopotentials for the first row transition elements. *The Journal of Chemical Physics*, 86(2):866–872, 1987.
- [29] Weigend, F. and Ahlrichs, R. Balanced basis sets of split valance, triple zeta valance and quadruple zeta valance quality for H and Rn: design and assessment of accuracy, *Physical Chemistry Chemical Physics*, 7:3297, 2005
- [30] Schäfer, A., Horn, H. and Ahlrichs, R. Fully optimized contracted Gaussian basis sets for atoms Li to Kr. *The Journal of Chemical Physics*, 97(4):2571–2577, 1992.
- [31] Ralph, P. G. Chemical hardness and density functional Theory, *Journal of Chemical Sciences*, 117:369, 2005.