

# MAGNETOSTRUCTURAL STUDY OF TRANSITION METAL COMPLEXES AND CLUSTERS BY COMPUTATIONAL METHODS

## Abstract

Transition metal ions with unpaired electrons exhibit a rich variety of spectroscopic phenomena. They serve as catalysts and as active site in metalloenzymes that are at the heart of most of the key biochemical processes such as respiration, photosynthesis or nitrogen fixation. Electron paramagnetic resonance (EPR) spectroscopy provides information about the oxidation and spin states as well as the coordination geometry and the ligands around the transition-metal ions in their respective complexes. EPR is the leading magnetic technique in order to obtain geometrical and electronic information about these systems. It yields unique information about the nature of open-shell ground state and its dependence on the chemical environment. The more intense ligand–ligand ( $\pi \rightarrow \pi^*$ ) band overshadows the d–d electronic transitions. This makes the spectroscopic data on the electronic properties due to the multiplet structure originating from  $d^n$  configuration of the transition metal rather scarce. In this respect Electronic Spin-Resonance (ESR) spectroscopy comes to rescue.

## Chapter 1: Introduction

This chapter describes the theory and background of magnetic parameters of transition metal complexes and clusters. The  $g$ -tensor and  $D$ -tensor are important parts of any EPR spectrum. They exhibit details about the radical species present. These two parameters and hyperfine coupling can provide wealth of information on the electronic and geometrical structure of molecules or solids with unpaired electrons. They allow us to enhance our understanding of electronic factors governing the observed spectra. From fundamental theory, the two physical factors contributing towards both the parameters, viz.,  $g$ -tensor and total  $D$ -tensor  $D_{Tot}$ , are: the direct dipole-dipole interaction of unpaired electrons, i.e., i) spin-spin interaction (SS) and ii) the spin-orbit coupling (SOC) of excited states into the ground state that introduces some angular momentum into the ground state (assumed orbitally nondegenerate) and which is being picked up by the spin of a second electron between the two contributions. In this chapter we have discussed the computational methods that we have used for calculations in this thesis. Also a brief discussion is done on the quantum mechanical methods which form the basis of our theoretical calculations.

## **Chapter 2: Zero field splitting in Mn (III) complexes: A comparative study of DFT base Coupled-Perturbed and Pederson–Khanna approaches**

In the present work we have carried out DFT studies on a series of Mn(III) complexes, numbered from (1 to 7). We have done a comparative study of the two SOC approaches viz., CP (coupled-perturbed) and PK (Pederson-Khanna) methods to estimate  $D_{SOC}$  that would lead to closer experimental D-tensor values of the complexes. We can conclude that the spin-spin part of the ZFS parameter is not negligible and account for only ~30% contribution to  $D_{Tot}$ . Also it is revealed in this study that the DFT method of CP, using any local and gradient-corrected functional like BP and def2-TZVP basis set for Mn(III) complexes for estimation of the ZFS parameters can give results in good agreement with the experimental values.

## **Chapter 3: A Systematic Approach to Find Suitable Basis Sets and Functionals for Better Prediction of Magnetic Parameters Using Cu(II) Complexes**

Copper complexes are known for exhibiting paramagnetic behaviour. We have taken mono and bidentate ligands bound Cu(II) complexes numbering (1 to 7) and tried to study the changes in the values of g-tensor in accordance with the different types of functionals used. We have taken four combinations of basis sets and functionals for each of the simpler complexes (1-7) Additionally, we have employed a relativistic approximation IORA for the Cu(II) bis(oxamato) complexes (8-13). It was found that or the simpler Cu(II) complexes (1-7) the basis set EPR-III gives value closer to the experimental results as compared to the def2-TZVP basis set. Another observation is that the hybrid functional B3LYP gives value closer to the experimental result than compared to the GGA functional of PW91. As for the Cu(II) bis(oxamato) complexes (8-13). The IORA method when paired with the NESC in the modified Dirac equation gives g-tensor values much closer to the experimental g-values.

## **Chapter 4: Regular Approximation Approach for Prediction of Magnetic Parameters in Co(II) Complexes and their Correlation with Chemical Reactivity**

Magnetostructural correlations form a basis for relationship between structure and reactivity of coordination complexes. We have studied four Co(II) complexes with  $[Co(Cl_2L_2)]$  formation where L is heterocyclic N donor ligands numbered from (1 to 4). We have found the role of heteroatom N and Cl in this case, in magnetism and reactivity. So we have also

done Mulliken population analysis and Frontier Molecular Orbital (FMO) study. Also a comparison of IORA and the ZORA method are done while doing the single point calculation for g-tensor and D-tensor. It was found that the g-shifts are dominated by the  $\Delta g_{\text{iso}}$  contributions which is the average g-value in all the three axes. Combinations of the QRO method as well as the relativistic approach IORA shows g-tensor values close to the experimentally obtained results. From this work we can get an insight that g-tensor values are directly related to the reactivity of a mononuclear complex.

### **Chapter 5: An Investigative Study for Estimation of Zero Field Splitting and Hyperfine Coupling in Co(II) Complexes using *ab initio* CASSCF Method**

Besides DFT, *ab initio* method also plays vital role in prediction of magnetic parameters. We have studied four Co(II) complexes with heterodentate ligands having N, P and halide atoms and calculated their D-tensor and hyperfine coupling constant, A. We have preferred the *ab initio* CASSCF method in this work for D-tensor as it is fully variational which renders the calculation of analytical gradients very easy. In literature it was reported that the phosphine containing complexes  $\text{Co}(\text{PPh}_3)_2\text{X}_2$  have negative D-tensor values. There is successive increase in the magnitude of D while coming from  $\text{CoN}_2\text{X}_2$  to  $\text{Co}(\text{PPh}_3)_2\text{X}_2$ . This trend is similar to that observed in  $\text{TpNiX}$  series ( $D = +3.93, 11.43, 22.81 \text{ cm}^{-1}$ , for  $X = \text{Cl, Br, I}$ , respectively). So we have taken these complexes for investigation of the effect of ligand environment on the magnetic parameters. In conclusion it is seen that there is significant magnetic anisotropy by spin-orbit coupling in the  $\text{Co}(\text{PPh}_3)_2\text{X}_2$  complexes. The significant D values is attributed to the relatively low-lying excited states in case of these tetrahedrally coordinated geometries, that enhances the second order perturbations of the ground state via spin-orbit coupling. The greater magnitude of the D-tensor in the  $\text{Co}(\text{PPh}_3)_2\text{X}_2$  complexes implies large energy gaps between the  $\pm 3/2$  and  $\pm 1/2 M_S$  levels for spin reversal.

### **Chapter 6: Density Functional Study of Magnetic Parameters in $(\text{NiO})_n$ Nanoclusters**

A series of  $(\text{NiO})_n$  (where  $n=2-7$ ) nanoclusters were pre-screened in KLMC and then refined at DFT level in FHI-aims program package. Global based optimization routines (evolutionary and stochastic quenching algorithms) are implemented within the in-house KLMC which can locate the DFT energy minima for this series of  $(\text{NiO})_n$  nanoclusters. Subsequently, we have done single point density functional studies of their magnetic properties which include calculating their corresponding zero-field splitting parameters, i.e., D-tensor and g-tensor

values. It is compiled in our study that the D-tensors calculated are very high and most of them have positive D-values while there is significant deviation from the free electron g-tensor value.

## **Chapter 7: Conclusion and Future Prospects**

The main objective of the above studies was to find a suitable computational method that would help in the prediction of magnetic parameters like g-tensor, D-tensor and hyperfine coupling constant theoretically based on the coordinating environment surrounding a metal ion. Further studies can be done to find more accurate computational methods for prediction of magnetic parameters. In future many additional challenges like treatment of the g-tensor, D-tensor or the hyperfine coupling constant in anisotropic exchange resulting from spin-orbit coupling or spin-spin coupling must be dealt with. While employing CASSCF method for multinuclear complexes active space should be more precisely calculated for better results.