

CHAPTER 7

Conclusion

Abstract

This chapter presents a general and comprehensive conclusion of all the chapters.

This chapter deals with the general conclusive remarks drawn from the previous chapters. The first chapter provides a brief introduction to the origin and advancement of research in aromaticity, magnetic exchange coupling and magnetic anisotropy of the metal based systems. The development of the theory of aromaticity with the advent of the synthesis of new materials based on transition metals, heavy metals or alkaline earth metals have been discussed. The origin and the chronological advancement of the theory and synthetic research of metal complexes have been elaborated with special emphasis on the application of the magnetic materials as data storage devices and nanomagnets. Finally, the role of theoretical research in the progression of the field of magnetism is explained.

The second chapter presents a brief theoretical framework of the measurements of aromaticity based on energetic, magnetic and structural criteria are discussed. Some of the methods that are utilised in this thesis to quantify aromaticity are explained in detail. The estimation of magnetic exchange coupling constant based on density functional theory based methodology is explicated elaborately. The most popular broken symmetry approach and spin flip approach are elucidated thoroughly. Finally, the estimation of magnetic anisotropy through density functional methods is enlightened. The Pederson-Khanna (PK) method and the Neese methods of quantification of axial and rhombic ZFS parameter D are also explained.

Chapter three explains the change in the aromaticity and energy profile of the singlet state of Mg_3Na_2 molecule and gradual attainment of the BS state with an increase in Na– Mg_3 distance. Near the ground state, Mg atoms are held together by a pair of π -bonding electrons onto which Na^+ ions are impregnated. The circulation of π -electron cloud above and below the Mg_3 plane also contributes to the σ - and π -aromaticity of the molecule. However, in this situation, the stability due to aromaticity has to compete with the Pauli repulsion. When the Na ions move away from Mg_3 plane with all the charge density, the aromaticity is also gradually lost, though the system gets stability due to decrease in Pauli repulsion. At a critical value (~ 4.33 Å) of Na– Mg_3 distance, the Pauli repulsion approaches a minimum due to localization of charge density on Na atoms above and below the plane. This charge accumulation on Na atoms makes these neutral doublet species with up-spin polarization at one Na and down-spin at another. The spins on Na atoms undergo superexchange. The stabilization due to superexchange and lowering of Pauli repulsion partly compensates the loss in bonding energy in the molecule for the charge migration to Na atoms. The Na spins are found to be engaged in antiferromagnetic interaction which gradually decreases with an increase in Na– Mg_3 separation.

Chapter four explains that the phenomenon of charge transfer (CT) is of paramount impact in guiding the courses of several magnetic processes. In the present study, the charge transfer process is also found effective in governing the magnetic behavior of metallocene based charge transfer complexes. A recently synthesized system, $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ is taken as the representative MBCTC to explore the influence of charge transfer on the magnetic behavior of such donor–acceptor complexes. Anderson in his pioneering work ascribed charge transfer as the origin of kinetic exchange and correlated this exchange with the second order perturbation energy for such charge transfer. In a recent work, using this approach of

Anderson, the coupling constant is parameterized with spin population. However, through bond charge transfer in a superexchange process is accounted for with the help of a newly developed equation in this chapter. On the contrary, NBO analysis for the present system clarifies a zero overlap status in between the donor and acceptor, which necessitates the tunnelling of electron in its journey from the donor to the acceptor. The electron tunnelling matrix element (H_{DA}) integral, is evaluated from the zeroth order eigenvalues of pure donor and acceptor at the transition state of the electron transfer process. The exchange coupling constant (J_T), obtained in this way is well in agreement with J , the coupling constant derived through well-known spin projection technique of Yamaguchi. The charge transfer interaction happens to be the central in such type of complexes where the magnetic interaction begins after the charge dislocates from the donor to the acceptor creating one magnetic site at the acceptor. The topological difference of V-pair and H-pair leads to the possibility of concurrent and competitive exchange interactions at different directions. In V-pair, the intervening Cp* ring assists the transfer of electron from metal to acceptor unit and hence there operates the superexchange process in this direction. In the other direction, the donor and acceptor are far separated and there is no such aid for the spins to be transferred from the donor to the acceptor. Hence the direct exchange process becomes only viable in H-pair. From the comparison of the coupling constant values, the superexchange interaction is found dominant in between two exchange processes in $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$. Since, the weak interaction in the horizontal direction takes a decisive role to render overall magnetic ordering; the V- and H-pairs are simultaneously taken into account. This situation opens up the possibility of several exchange interactions among multiple magnetic sites, which is estimated through a newly developed computational scheme, referred to as dummy approach within the text. The coupling constant value for the V-pair, obtained through this approach is found to be very low compared to the previous value, where only the V-pair is considered. The drastic decrease in the J value through dummy approach is attributed to the interchain interaction. The coexistence of competitive superexchange and direct exchange in this truncated model replicates the bulk behavior. It has been of optimal challenge to investigate the nature of magnetism in a crystal system. The best way to mimic the real network of spins of a cluster demands the application of periodic boundary condition. The PBC can treat systems in bulk condition with much less computational effort without taking the finite size-effect and border-effect. Our calculation clearly shows that the magnetic interaction in one dimensional periodic lattice of such kind of system in the vertical direction is antiferromagnetic and the extent of magnetism is too low. Moreover, it is interesting to note that the FM system turns into an AFM one with imposition of periodic boundary condition. This change over in the magnetic status of the system is explained with the rearrangement of the density of states in $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$. In this condition, there occurs a simultaneous higher and lower energy shifts in the donor and acceptor orbitals respectively and the donor-acceptor overlap integral gains a non-zero value, which is otherwise zero in the system. This lift in energy of the d -states is also supported from the easy dispersion of alpha spin to the Cp* ligand orbital. Hence, this situation facilitates electron delocalization and results a lower Hubbard U value. As a consequence of all these facts the $[\text{Cr}(\text{Cp}^*)_2][\text{ETCE}]$ which exhibits ferromagnetic coupling in the single D^+A^- pair, turns into an antiferromagnetic system in the periodic condition along vertical direction. However, the convolution of different exchanges

pervading the crystal makes it a weak ferromagnet. An extended review on MBCTC divulges that there is a delicate balance in the sign of coupling constant in horizontal direction. This weak, still competing magnetic interaction is regarded as the principle criterion for metamagnetism. However, this work suggests a delicate poise of magnetic interaction in the vertical direction as well.

In chapter five, the magnetic anisotropy property of a series of octahedral Cr(III) complexes is studied. It has been shown that π -donor and π -acceptor ligands, in the axial position of the octahedral complexes, have different effects on the magnetic anisotropy of the complexes. The interaction of the ligands with the metal d -orbitals gives rise to two different situations responsible for this kind of switch in the ZFS parameter. The π -donor ligands play a role in making the magnitude of ZFS larger with an increased π -donation from the halide ligands, while a π -acceptor ligand causes the anisotropy property to be of easy-axis type ($D < 0$). Moreover, a π -acceptor ligand in both the axial positions imparts single molecular magnetic nature to the system having an easy-axis of the magnetic anisotropy. An increased donation from the equatorial positions is seen to enhance the magnitude of easy axis type magnetic anisotropy. This can be attributed to the increased π -accepting efficiency of the axial ligands due to an enhanced metallic electron density, pushed by the equatorial ligands. On the basis of the above observations regarding the ligand replacement, octahedral Cr(III) complexes can be designed in such a way that it can meet our desired anisotropy characteristics. The NLO response is found to vary with π -donation similarly as the magnetic anisotropy. The second-order NLO response, β , has been related to the magnetic anisotropy in the case of the non-centrosymmetric octahedral complexes, where we can see that the NLO response can lead us to good anticipation of magnetic anisotropy. From the systematic DFT study with these octahedral complexes, a clear understanding about the influence of the ligands on modulating the magnetic anisotropy of the Cr(III) complexes is possible. For convenience, we perform a few numerical experimentations. The D value for $[\text{CrBr}_4(\text{CN})_2]^{3-}$, is -0.69 cm^{-1} . We calculate the ZFS parameter for $[\text{CrBr}_4(\text{CO})_2]^-$, which comes out to be -2.51 cm^{-1} . Now relying on the above method of prediction, we design a complex of formula $[\text{CrBr}_4(\text{CN})(\text{CO})]^{2-}$ and expect the D value to be in between -0.69 cm^{-1} and -2.51 cm^{-1} and get a value of -0.94 cm^{-1} . Thus, from this observation, a general conclusion can be drawn that the anisotropy of such metal complexes is greatly controlled by the ligands. To summarize, this work explicates a simple application of DFT to calculate anisotropy parameters in metal complexes to devise a rule of thumb for the occurrence of SMM behaviour in such complexes.

Emerging interest in mononuclear complexes, in comparison to polynuclear ones, has meant that the field of quantum magnets has turned to tuning of the ZFS parameter D through structural modification or external aids. Chapter six contemplated the magnetic anisotropy of an octahedral Co^{II} complex, namely, $[\text{Co}^{\text{II}}(\text{dmphen})_2(\text{NCS})_2]$, in connection with the tunability of ZFS parameter D by exploiting an electric field as an external stimuli. Previously, it was shown that the presence of a π -accepting ligand in the axial position of an octahedral complex could result in magnetization of the molecular magnetic dipole along a specific direction. The external electric field in the present situation assisted such metal-to-

ligand charge transfer and led to a switch over in the anisotropic characteristics. A spin-Hall spatial spin separation was also observed due to modulation in the Rashba spin-orbit coupling in a single molecule, for the first time, rather than in mesoscopic systems.