

Chapter 6

Summary and Conclusion

Presence of uniaxial magnetic anisotropy is widely recognized as the most essential criterion for observing slow relaxation of magnetization in molecular species. Magnetic anisotropy originates from zero field splitting (ZFS) which itself occur due to the interplay of spin-orbit and spin-spin coupling. Large uniaxial magnetic anisotropy in lanthanide complexes has been primarily attributed to unquenched orbital angular momentum in ground electronic state which leads to in-state SOC. However, in high coordinate transition metal species, the only possibility to induce magnetic anisotropy is via spin-orbit coupling of ground electronic state with excited electronic states possessing unquenched orbital angular momentum. Thus, the extent of out-of-state spin orbit coupling is highly influenced by the difference in energy between ground state with excited states involved in SOC. Therefore, judicious choice of coordination environment around the central metal ion should allow us to modulate the magnetic anisotropy in a rational and predetermined fashion.

In this thesis, systematic analysis of magnetic anisotropy in a series of pentagonal bipyramidal (PBP) complexes prepared from an acyclic pentadentate bis-hydrazone ligand, 2,6-diacetylpyridine bis(benzoylhydrazone) (H_2L) is elaborated. Several PBP complexes Mn(II), Co(II) and Ni(II) have been prepared using the bis-hydrazone ligand and the coordination environment of these complexes are subtly different from each other. Further, variable temperature magnetization measurements of the polycrystalline samples of these synthesized compounds along with DFT calculations have been performed to estimate the nature as well as magnitude of magnetic anisotropy. Apart from the above, the PBP Mn(II) complexes were used as building block to assemble cyano bridged heteronuclear species using different cyanometallates and their magnetostructural correlation was performed.

A general introduction on the origin of single molecular magnetic behaviour is presented in chapter 1. Further, the relevance of magnetic anisotropy in observing slow relaxation of magnetization at high T_b is also described. A review of magnetic anisotropy of transition metal complexes with two-coordinate to seven-coordinate geometries have been presented. The role of geometry as well as coordination environment in modulating the magnetic anisotropy has been described in this chapter. Based on these discussions the objectives of the work described herein are presented in this chapter.

In chapter 2, we have reported the synthesis, characterization, crystal structures and magnetization studies of four PBP Mn(II) complexes $[\text{Mn}(\text{H}_2\text{L})(\text{SCN})_2] \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Mn}(\text{HL})(\text{H}_2\text{O})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Mn}(\text{HL})(\text{H}_2\text{O})_2]\text{ClO}_4$ (**3**) and $[\text{Mn}(\text{L})(\text{H}_2\text{O})_2]$ (**4**). Single crystal X-ray structure determinations of all four complexes, **1-4** reveal that the coordination environments of the four complexes were subtly different from each other. The acyclic pentadentate bis hydrazone ligand H_2L is present in neutral form in compound **1** while in compounds **2** and **3**, it is monoanionic. The dianionic form of the ligand is observed in compound **4**. The ZFS parameters of compounds **1-4** have been determined both experimentally and theoretically. In general, good agreement is observed between the experimentally determined ZFS parameter and theoretically estimated ZFS parameters. Results presented herein indicate that the value of ZFS in PBP Mn(II) complexes strongly depend on the coordination environment. As observed for five and six coordinate Mn(II)-halide complexes, the ZFS of PBP Mn(II) complexes also increase with increasing covalency of axial metal-ligand bond. In spite of identical equatorial ligand environment in both compounds **2** and **3**, the large difference in ZFS between these two compounds can be attributed to the larger covalency of Mn(II)-chloride bond in compound **2** as compared to Mn(II)-O(H_2O) bond in compound **3**. Accordingly, presence of two Mn(II)-NCS bond with reasonable covalency accounts for the rather large ZFS observed in compound **1**. However, the ZFS value observed in compound **4** is large and negative which can be possibly attributed to the enhanced covalency of equatorial metal-ligand bonds due to the dianionic nature of the planar pentadentate ligand. The SOD activity of the rigid PBP Mn(II) systems, **1-4** have been evaluated by using an indirect Nitro Blue Tetrazolium (NBT) assay and it is observed that compounds **3** and **4** can efficiently decompose superoxide and the IC_{50} values are comparable to those observed in case of PBP Mn(II) complexes reported earlier.

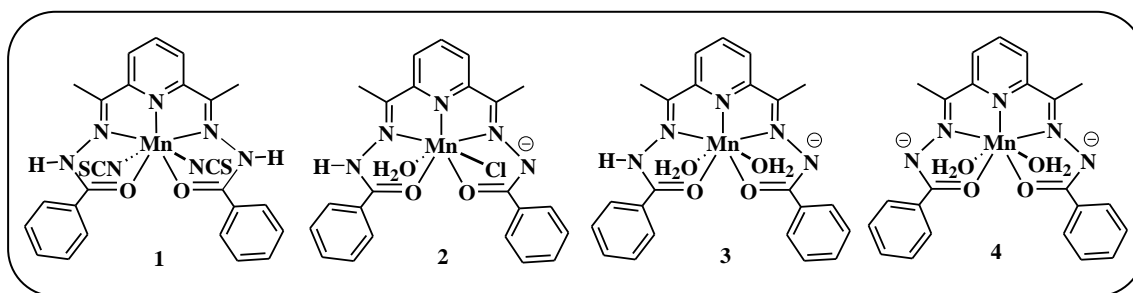


Chart 6.1. Chemical structures of compounds **1-4**

In chapter 3, synthesis and characterization of six PBP Co(II) complex of the bis-hydrazone ligand, $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**5**), $[\text{Co}(\text{H}_2\text{L})(\text{SCN})_2] \cdot 3\text{H}_2\text{O}$ (**6**), $[\text{Co}(\text{H}_2\text{L})(\text{SCN})_2] \cdot 4\text{H}_2\text{O}$ (**7**), $[\text{Co}(\text{HL})(\text{SCN})(\text{H}_2\text{O})]$ (**8**), $[\text{Co}(\text{HL})(\text{H}_2\text{O})_2](\text{NO}_3) \cdot \text{H}_2\text{O}$ (**9**) and $[\text{Co}(\text{L})(\text{H}_2\text{O})_2]$ (**10**) are elaborated. The ZFS value for all the compounds were determined using magnetization measurements and the experimental results have been rationalized with the help of DFT based theoretical calculations. Moreover, superoxide dismutase activity of these compounds has been studied spectrophotometrically using indirect nitro blue tetrazolium (NBT) assay.

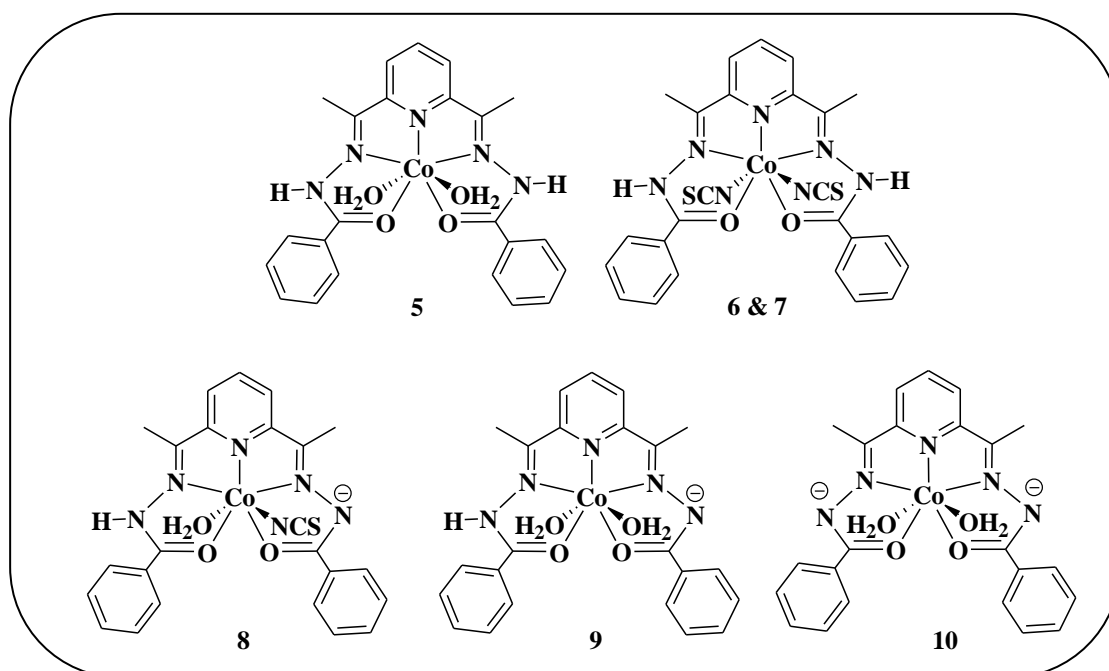


Chart 6.2. Chemical structures of compounds **5-10**

The origin of this large positive D parameter in PBP Co(II) complexes lies in SOC stemming from the mixing of the ground electronic level with two excited electronic levels. Thus, in principle it should be possible to control magnetic anisotropy by tuning the mixing of ground electronic state with the excited electronic states. Results presented in chapter 3 support earlier theoretical findings that the second order spin-orbit perturbation mediated control of magnetic anisotropy is possible by appropriate modulation of coordination environment. It is observed that either by employing a better σ -donor apical ligand or by using a symmetric pentadentate equatorial ligand, it is possible to significantly decrease the positive contribution to D parameter. Earlier approaches to modulate axial ZFS parameter through modification of coordination

environment primarily relied on covalent character of metal-ligand linkages. However, for PBP Co(II)-H₂L complexes reported so far no such trend based on hard/soft character of the donor ligands is observed. Instead, the present approach of modulating magnetic anisotropy is based on tuning the contribution of second order perturbation to SOC in a predetermined fashion by modifying the energy of the excited levels. Thus, even in high coordinate species with no first order perturbation to magnetic anisotropy there is a possibility to induce magnetic anisotropy by appropriately modulating the coordination environment. Proliferation of the present approach is anticipated to open fascinating frontiers for synthetic chemist to induce magnetic anisotropy in high coordinate species.

The syntheses, characterization, crystal structures and magnetization measurements of four PBP Ni(II) complexes, [Ni(H₂L)(SCN)₂].3H₂O (**11**), [Ni(HL)(SCN)(H₂O)] (**12**), [Ni(H₂L₁)(SCN)₂].2H₂O (**13**) and [Ni(H₂L₁)(im)₂](NO₃)₂ (**14**) (H₂L₁: 2,6-diacetylpyridine bis- semicarbazone) have been described in chapter 4.

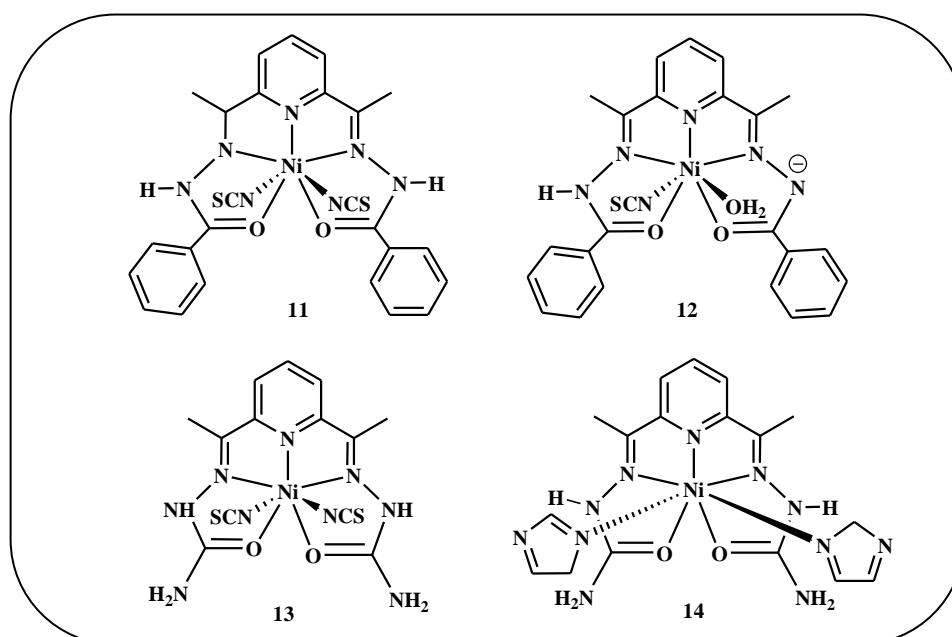


Chart 6.3. Chemical structures of compounds **11-14**

Single crystal X-ray structure determinations of all four complexes, **11-14** reveal that the coordination environments of the four complexes were subtly different from each other. The acyclic pentadentate bis-hydrazone ligand H₂L is neutral in compound **11** while in compounds **12**, it is monoanionic. Compounds **13** and **14** were synthesized

using another acyclic bis-semicarbazone ligand H_2L_1 . The ligand H_2L_1 in compound **13** is in neutral form whereas in compound **14**, it is present in monoanionic form.

The ZFS parameters of compounds **11-14** have been determined experimentally. Contrary to our anticipation, it has been found that modification of the coordination environment around the Ni(II) center do not change the value of D appreciably in these compounds. Moreover, the SOD activity of compounds **11-14** have been evaluated by using an indirect assay and it is observed that due to the absence labile aquo ligands coordinated to the axial sites of PBP Ni(II) center, these compounds could not decompose superoxide.

In chapter 5, results of the reaction of a PBP Mn(II) precursor, $[Mn(H_2L)(H_2O)Cl]Cl$ with cyanometallate linkers have been presented. It was anticipated that the labile axial ligands present in $[Mn(H_2L)(H_2O)Cl]Cl$ can be easily replaced by cyanometallates and this should lead to the formation of heterometallic cyano bridged architectures. In principle, structures as well as nuclearity of such heterometallic aggregates should primarily rely on the charge of the precursors. Based on this principle of electroneutrality, a range of structural motifs have been isolated by the reaction of the PBP Mn(II) precursor, $[Mn(H_2L)(H_2O)Cl]Cl$ with the cyanometallate linkers having different charge, e.g. $[Fe(CN)_5(NO)]^{2-}$ and $[Fe(CN)_6]^{3-}$. Results presented herein show that intricate control over the self-assembly process can also be achieved by proper choice of reaction medium. Reaction of $[Mn(H_2L)(H_2O)Cl]Cl$ with $[Fe(CN)_5(NO)]^{3-}$ in aqueous methanolic medium immediately leads to the formation of an amorphous solid, which is insoluble in common organic solvents. Presence of an additional anion with coordinating ability can overwhelmingly influence the self-assembly process and results described here suggest that presence of KSCN avert formation of polymeric structure. Therefore, in order to prevent formation of polymeric material, we carried out the reaction of $[Mn(H_2L)(H_2O)Cl]Cl$ with $[Fe(CN)_5(NO)]^{3-}$ in the presence of KSCN. Presence of KSCN hindered the coordination of cyanometallate with the PBP Mn(II) and simple binuclear salt, $[Mn(H_2L)(H_2O)_2][Fe(CN)_5(NO)].H_2O$ (**15**) of the PBP Mn(II) complex ion with the nitroprusside anion was isolated. Interestingly, it has been observed that presence of excess water in the above reaction impedes isolation of the ionic compound **15** but lead to the crystallization of a neutral bimetallic species $[\{Mn(H_2L)\}\{Fe(CN)_5(NO)\}]$ (**16**). One of the axial sites of the PBP Mn(II) ion is occupied by cyano group of nitroprusside ion and this eventually leads to the formation

of the dinuclear heterometallic structure in compound **16**. Moreover, when the reaction leading to the formation of compound **16** was carried out in the absence of KSCN, a 1D polymeric species, $[\{\text{Mn}(\text{H}_2\text{L})\}\{\text{Fe}(\text{CN})_5(\text{NO})\}\cdot(\text{H}_2\text{O})_{0.75}]_n$ (**17**) is formed where both the axial sites of the PBP Mn(II) ion are occupied by cyano groups of nitroprusside ion.

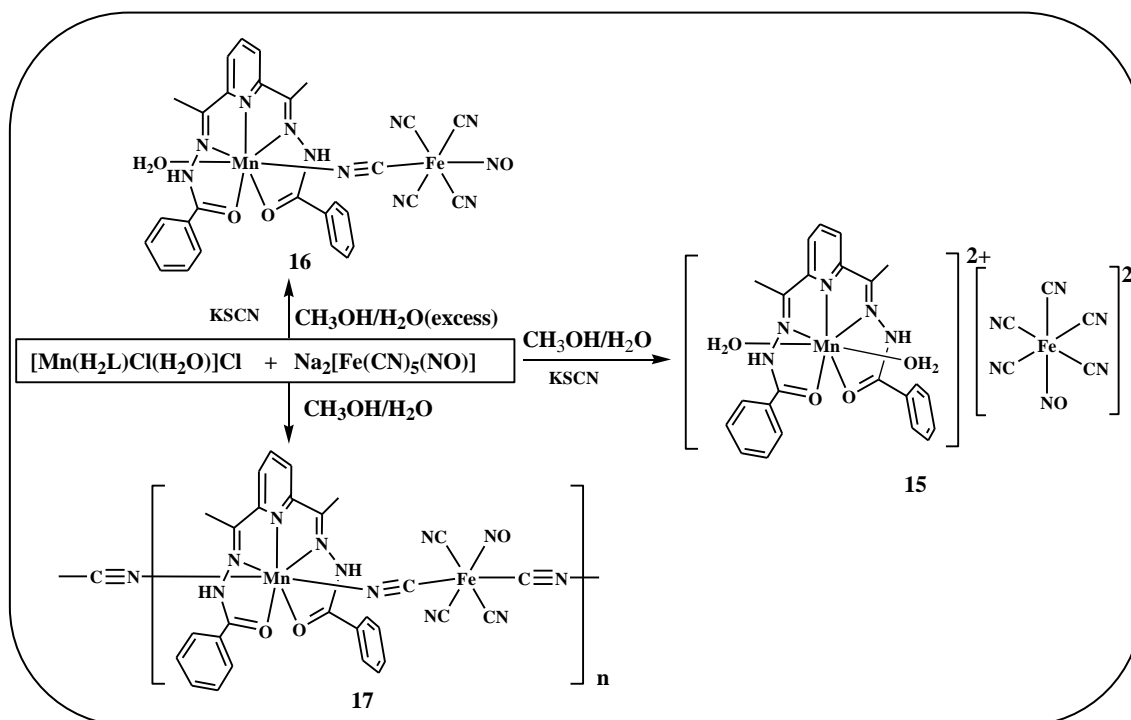


Chart 6.4. Chemical structures of compounds **15-17**

The structural motifs **15-17** lack cooperative magnetic properties since the nitroprusside anion is diamagnetic in nature. However, one can anticipate assembling cyanometallate architectures with intriguing magnetic features simply by using paramagnetic cyanometallate precursors. Therefore, reaction of PBP Mn(II) precursor, $[\text{MnL}(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ was investigated with a paramagnetic cyanometallate ion, $[\text{Fe}(\text{CN})_6]^{3-}$ and two new cyano bridged Fe(III)-Mn(II) heterometallic aggregates, $[\{\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})\}_2\{\text{Mn}(\text{H}_2\text{L})\}\{\text{Fe}(\text{CN})_6\}_2]\cdot 9\text{H}_2\text{O}$ (**18**) and $[\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})_2]_2[\{\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})\}_2\{\text{Fe}(\text{CN})_6\}][\{\text{Mn}(\text{H}_2\text{L})\}_2\{\text{Fe}(\text{CN})_6\}_3]\cdot 13\text{H}_2\text{O}$ (**19**) are prepared. Single crystal X-ray diffraction analysis was performed to unambiguously determine the structures of both the heteronuclear complexes **18** and **19**. The pentanuclear cyano bridged structural architecture observed in compound **18** is quite prevalent, while the structure of decanuclear compound **19** is unique due to the presence of four isolated motifs in compound **19**. Investigation of magnetic properties

reveal that both the complexes **18** & **19** have irregular spin state structures and antiferromagnetic interactions are operative between the adjacent spin carriers. Controlled aggregation of cyanometallates in a predetermined fashion will allow us to explore the potential of these species in building molecular magnets with better characteristics.

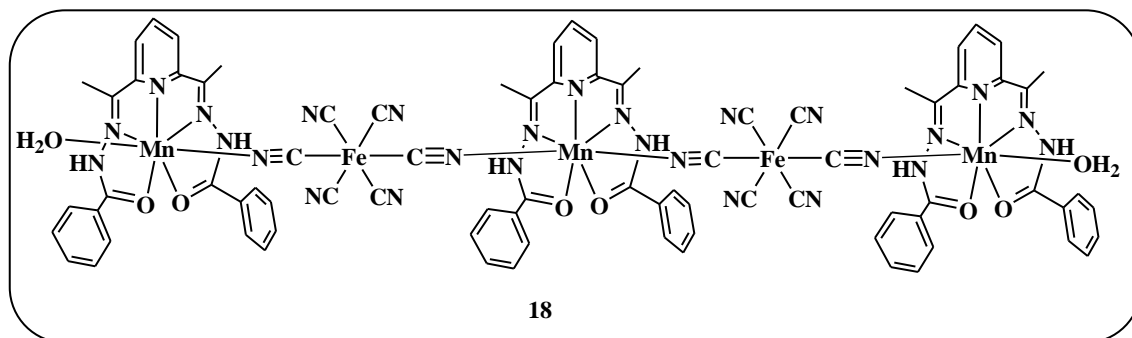


Chart 6.5. Chemical structure of compound **18**

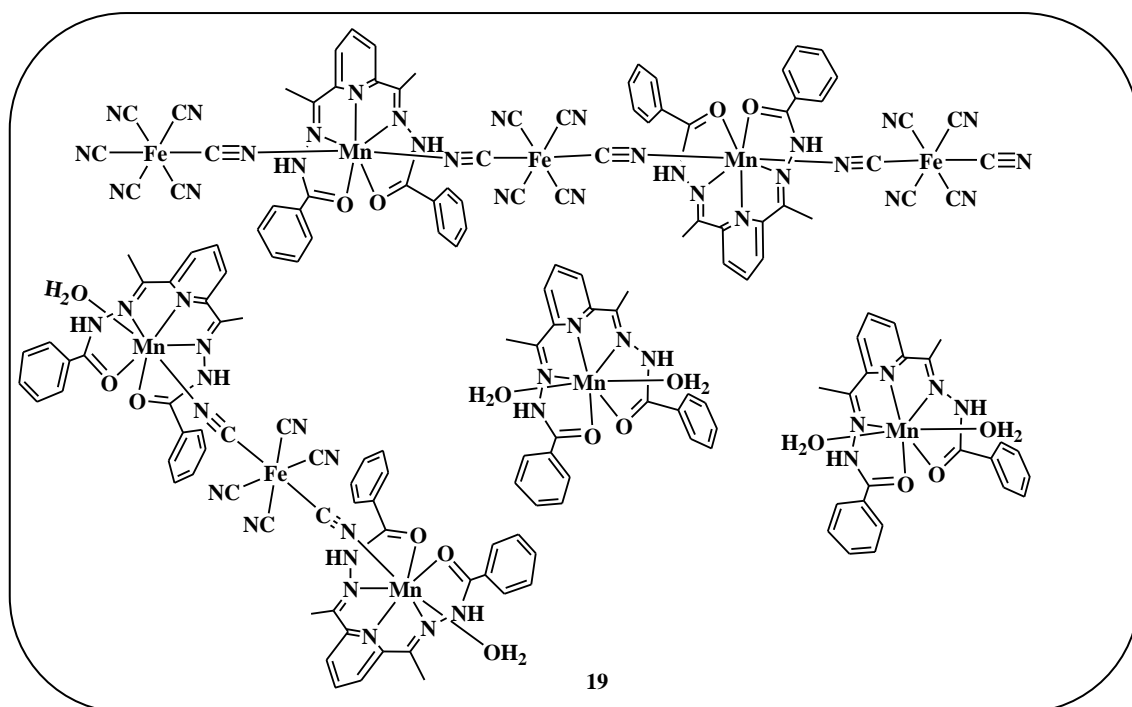


Chart 6.6. Chemical structure of compound **19**

Thus, the present thesis successfully addressed a key issue involved in the development of high T_b nanomagnets and several noteworthy milestones are achieved during the course of this work. Initial investigations primarily focussed on the synthesis of PBP complexes of Mn(II), Co(II) and Ni(II) using a bis-hydrazone ligand. Thereafter, all

these complexes are characterized by using analytical and spectroscopic studies. Single crystal X-ray diffraction measurements were performed to unambiguously establish the structure of all the compounds prepared and in each case the central metal ion is found to occupy PBP geometry. The equatorial coordination sites of all the PBP complexes are occupied by the bis-hydrazone ligand. However, the planar pentadentate bis-hydrazone ligand contains two acidic N-H protons and in many cases, the monoanionic as well as dianionic form of the ligand was observed. Thus, although the local geometry around the central metal ion is invariably PBP in all the complexes, both the equatorial as well as axial coordination environments are varied in a subtle yet systematic manner.

Temperature dependence of magnetization studies carried out under static dc field of 1000 Oe revealed that all the Mn(II), Co(II) and Ni(II) PBP complexes are paramagnetic in nature. Moreover, the sharp decrease in $\chi_{\text{M}}T$ product in low temperature region was attributed to ZFS. Nevertheless, isothermal field dependence of magnetization studies was performed for all these PBP complexes. Inspection of the reduced magnetization plots revealed the presence of weak but non-zero magnetic anisotropy in the Mn(II) complexes while significantly large magnetic anisotropy are present in Co(II) and Ni(II) complexes. Fitting of the field dependence of magnetization plots at different temperatures were performed to determine the value of ZFS values parameter for all the complexes. DFT calculations based on the coupled perturbed method was also performed for Mn(II) and Co(II) PBP complexes to evaluate D values and in all the cases good agreement of the calculated D values with the experimentally determined D values were observed. Correlation of the ZFS values for the PBP Mn(II) complexes reveal that complexes containing stronger σ -donor axial ligands have large positive D values while stronger equatorial ligand field led to negative D values.

Similarly for the PBP Co(II) complexes, increasing both the axial and equatorial ligand field strength led to lowering of the large positive D values generally observed in reported D_{5h} Co(II) system. The deviation of the ZFS parameter in PBP Co(II) complexes from the reported D values of D_{5h} Co(II) system can be easily rationalized with help of theoretical calculations performed earlier. Moreover, significant lowering of ZFS values of PBP Co(II) complexes were observed upon deviation of the local coordination geometry around the Co(II) center from ideal D_{5h} geometry. Lowering of

symmetry quenches the orbital angular momentum of the excited states involved in SOC and thereby reduces the D value significantly. However, in case of PBP Ni(II) complexes, no significant deviation in axial ZFS parameter was observed even when strong σ -donor axial ligands are used. Careful analysis of the excited states involved in out-of-state SOC revealed that energy of one of the excited state increases while that of another excited state decreases under the influence of stronger axial ligand field. Due to these two opposing effects, overall there is no appreciable deviation in D parameter on changing the axial ligand field.

The presence of labile axial ligands on the PBP complexes synthesized herein provided us an appealing opportunity to develop heterometallic species by replacing the axial sites with suitable metalloligands. In view of the fascinating array of intriguing magnetic properties displayed by cyano bridged polymetallic aggregates we employed cyanometallate bridging groups to interlink PBP species. Previous studies have established that the self-assembling process between cyanometallate anion and cationic 3d building block is primarily governed by the charge on both species. Based on the principle of electroneutrality, a range of structural motifs have been isolated by varying the charge on the motifs. Results presented herein show that intricate control over the self-assembly process can be achieved by proper choice of reaction medium. Excess water present in the reaction medium impedes isolation of an ionic compound **15** but lead to the crystallization of a neutral bimetallic species **16**. Moreover, presence of an additional anion with coordinating ability can overwhelmingly influence the self-assembly process. Results described here suggest that presence of KSCN as well as NaClO₄ can avert formation of polymeric structure. The magnetic features of the heterometallic species were investigated by using low temperature magnetization studies and the extent of magnetic exchange interaction was also deduced by fitting the magnetization plots.

Even though several important milestones have been achieved and important generalization for improving ZFS of PBP complexes have been deduced during the course of this thesis, several important aspects have remained unaddressed primarily due to the constrain of time and lack of instrumentation facilities. The ZFS parameters of the PBP complexes reported herein are derived from magnetization studies supported by DFT based calculations. It is widely acknowledged that high field EPR studies are important to derive the magnitude as well as sign of ZFS parameter

accurately, especially when the extent of magnetic anisotropy is high. The ZFS values of the species reported herein are reasonably small and there is good agreement between the theoretically derived values with the experimental data. Nevertheless, we endeavour to perform high field EPR analysis of all the species reported here in the near future. Further, slight variation of the geometric features of the PBP complexes are found to influence the ZFS parameter, particularly in case of PBP Co(II) complexes. Therefore, in order to compare the influence of coordination environment on the ZFS values, species with identical geometric features must be investigated. In view of the above, it is important to prepare more such PBP complexes which will allow us to efficiently compare the ZFS values of species with identical geometric features. It has recently emerged that several transition metal ions show exceedingly large magnetic anisotropy in few other geometries e.g. tetrahedral, trigonal bipyramidal, etc. Moreover, the origin of magnetic anisotropy in all these cases is attributed to out-of-state SOC of the ground electronic state with excited states. Thus, the present approach to modulate magnetic anisotropy can also be extended to these geometries and thus deduce effective prescriptions to assemble transition metal based SMMs with large energy barrier for magnetization reversal. Our research group is currently exploring these fascinating frontiers and thus contribute towards development of high T_b nano-magnets.

Appendix A: List of publications

- [1] Dey, M. and Gogoi, N. Geometry-Mediated Enhancement of Single-Ion Anisotropy: A Route to Single-Molecule Magnets with a High Blocking Temperature. *Angewandte Chemie International Edition*, 52(49): 12780-12782, 2013.
- [2] Dey, M., Sarma, B., and Gogoi, N. Coligand Promoted Controlled Assembly of Hierarchical Heterobimetallic Nitroprusside Based Aggregates. *Zeitschrift für Anorganische und Allgemeine Chemie*, 640(14): 2962-2967, 2014.
- [3] Dey, M., Dutta, S., Sarma, B., Deka, R.C. and Gogoi, N. Modulation of the coordination environment: a convenient approach to tailor magnetic anisotropy in seven coordinate Co (II) complexes. *Chemical Communications*, 52(4): 753-756, 2016.
- [4] Dey, M., Goswami, A. and Gogoi, N. Surprises from an old reaction: a new 1-D heterometallic tris (pyridine-2-aldoximato) nickel (II)-sodium complex. *Transition Metal Chemistry*, 41(5): 509-516, 2016.
- [5] Dey, M., Sarma, B. and Gogoi, N. Cyano-bridged heterometallic Mn(II)-Fe(III) aggregates: Synthesis, structure and magnetic properties. *Inorganica Chimica Acta*, 469: 20-24, 2018.

Appendix B: Conferences, Seminars, Workshops attended and Posters presented

1. Attended Science Academies Lecture Workshop on “Emerging Trends in Chemical Sciences” organized by the Department of Chemical Sciences, Tezpur University during 11-13 November 2016.
2. Attended Science Academies Lecture Workshop on “Magnetic and Optical Properties of Molecular Materials: Principles and Applications” organized by the Department of Chemical Sciences, Tezpur University during 19-21 October 2016.
3. Presented a Poster entitled “*Coordination Environment Mediated Tailoring of Magnetic Anisotropy in Seven Coordinate Co(II) and Ni(II) Complexes*” in Materials Research Society symposium “*Advanced Materials for Sustainable Applications*” and 27th Annual General Meeting of MRSI jointly organized by CSIR-North East Institute of Science and Technology, Jorhat and Indian Institute of Technology, Guwahati and Tezpur University, Tezpur from 18th to 20th February, 2016.
4. Presented a Poster entitled “*Tailoring Single Ion Magnetic Anisotropy of Seven Coordinate Complexes by Modulation of Coordination Environment*” in UGC-SAP National Seminar on “*Emerging Trends in Chemical Sciences-2015*” organized by Department of Chemistry, Gauhati University from 5th to 6th November, 2015.
5. Attended Industry-Academia Meet on “*Consultative cum Awareness Meeting on Renewable Energy Application at North East India and Interaction of Finishing students with Industry*” organized by Department of Energy, Tezpur University from 3rd to 4th November, 2015.
6. Attended “*National Workshop on Crystallography Education 2014*” organized by Dept. of Chemistry, Gauhati University held on 8th November, 2014.
7. Presented a Poster entitled “*Hierarchical Heterometallic Aggregates Formed by Controlled Assembly of a Seven Coordinate Mn(II) Complex with Nitroprusside*” in “*8th Mid-Year CRSI National Symposium in Chemistry*” organized jointly by CSIR North-East Institute of Science and Technology, Jorhat and Tezpur University, Tezpur from 10th to 12th July, 2014.
8. Presented a Poster entitled “*Charge Assisted Assembling of Heterobimetallic Aggregates by Employing Magnetically Anisotropic Building Blocks*” in “*20th*

- National Magnetic Resonance Society Symposium cum Annual Meeting*” organized by Department of Chemical Sciences, Tezpur University from 2nd to 5th February, 2014.
9. Participated in “*Indo-Finnish Workshop on Green Chemistry*” organized by Dept. of Energy, Tezpur University from 13th to 14th December, 2013.
 10. Participated in the “*Science Academies Lecture Workshop on Modern Trends in Chemistry*” organized by Department of Chemical Sciences, Tezpur University from 20th to 22nd November, 2013.
 11. Presented a Poster entitled “*Exotic Coordination Geometry Driven Enhancement of Magnetic Anisotropy: An Emerging Approach for Building High T_b Nano-Magnets*” at “*Workshop on Spectroscopic Tools and their Applications*” organized by Department of Chemical Sciences, Tezpur University on 6th April, 2013.
 12. Participated in “*Indo-Finnish Symposium on Role of Catalyst on Production of Green Fuel*” organized by Department of Energy, Tezpur University on 1st February, 2013.
 13. Presented a Poster in “*National Seminar on Chemistry Education and Research and National Convention of Chemistry Teachers (NCCT-12)*” organized by Department of Chemistry, Gauhati University from 1st to 4th November, 2012.