

Abstract

Magnetic anisotropy is defined as the preferential alignment of spins in a particular direction. Species with large magnetic anisotropy undergoes easy magnetization along a particular axis/plane and resist reversal of magnetization along the other directions. When the spins are preferentially aligned along a plane, the plane is called easy plane of magnetization, whereas preferential alignment along a particular direction is called easy axis of magnetization. In magnetic materials, magnetic anisotropy manifests itself in the shape of hysteresis loop as well as determines the magnitude of coercive field. The freezing of magnetization reversal or magnetization blocking in super-paramagnetic substances is primarily attributed to the presence of an easy axis of magnetization. Similarly the key characteristics of low dimensional species e.g. single molecule magnets, single chain magnets, etc. showing slow relaxation of magnetization are also governed by the magnitude and directionality of magnetic anisotropy. In view of the above, tremendous research efforts are currently directed towards understanding the origin of magnetic anisotropy and thus devise rational routes to manipulate it in a premeditated or predetermined fashion.

Large uniaxial magnetic anisotropy is now widely recognized as an essential criterion for enhancement of blocking temperature of magnetization reversal in single molecular magnets (SMM) [1-5]. Since the last century, some molecular species have succeeded to demonstrate properties that were traditionally associated with inorganic materials, such as superconductivity, optical behaviour, magnetic susceptibility, quantum tunnelling of magnetization, etc. [6-8] Such species with a high-spin ground state and large easy axis of anisotropy, exhibit slow relaxation of magnetization below a certain temperature called blocking temperature (T_b) and are termed as Single Molecular Magnets (SMM) [9]. They behave like tiny bar magnets. In 1993, Dante Gatteschi and co-workers reported the first SMM, which is a dodecanuclear mixed valent Mn(III)/Mn(IV) cluster, $[\text{Mn}_{12}\text{O}_{12}(\text{COOCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ (Mn_{12}) [10] (Figure 1).

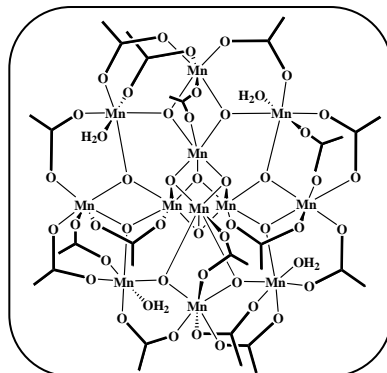


Figure 1. Structure of $[\text{Mn}_{12}\text{O}_{12}(\text{COOCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ (Mn_{12}).

The antiferromagnetic coupling between $S=3/2$ spins of Mn^{IV} and $S=2$ spin of Mn^{III} ions in Mn_{12} leads to a $S=10$ ground spin state. Due to zero field splitting (ZFS), the $S=10$ ground state splits into 21 ($M_s = +10$ to $M_s = -10$) microstates (Figure 2) [11]. Each level has an energy $E(m_s) = m_s^2 D$, where m_s is the spin projection quantum number and D is the axial zero field splitting parameter. In presence of an external magnetic field, $H \neq 0$ the $M_s = -10$ state will have lower energy and consequently $M_s = -10$ (spin up) level will be more populated as compared to the $M_s = 10$ (spin down) level.

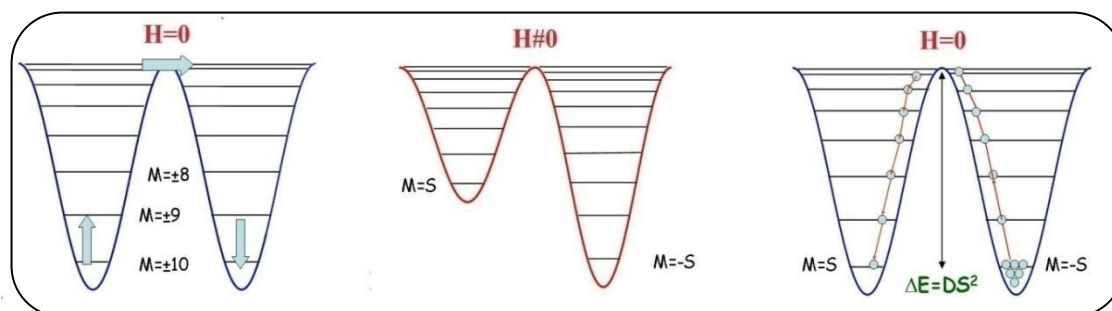


Figure 2. Double well potential energy diagram of Mn_{12} complex in the absence of magnetic field, on application of a magnetic field and on removal of the magnetic field again.

On switching off the external magnetic field at this stage, the $M_s = +10$ to $M_s = -10$ states once again become degenerate and therefore population in both the states tends to become equal. However, the negative axial zero field splitting create an energy barrier for magnetization reversal and thus the spin orientation reversal from spin-down ($M_s = -10$) to spin up ($M_s = +10$) state requires some energy [1]. If the energy barrier for magnetization reversal is appreciably large then the relaxation of magnetization shall be slow. The magnetization relaxation time can be expressed by the Boltzmann equation $\tau =$

$\tau_0 e^{\Delta E/KT}$, where ΔE is the energy barrier for magnetization reversal, K is the Boltzmann constant and T is temperature in absolute scale [12].

The energy barrier for magnetization reversal is given by the expression $\Delta E = DS^2$, where S is the spin of the system. For Mn_{12} complex, $\Delta E = 50 \text{ cm}^{-1}$ but at 300K, $KT = 208 \text{ cm}^{-1}$ ($K = 0.695 \text{ cm}^{-1}/K$) and therefore spontaneous relaxation of magnetization is observed at room temperature. However, if the temperature of the system is kept below 4K, slow relaxation of magnetization is observed. This threshold temperature limit is known as the blocking temperature (T_b). Raising the T_b of magnetization reversal in Single Molecule Magnets (SMMs) has remained a formidable challenge for their eventual practical application. Tremendous efforts are being devoted to rationalize the parameters governing the energy barrier of magnetization reversal (ΔE) in SMMs.

Quadratic dependence of ΔE on ground state spin initially led to the consideration that increasing S is an appealing route to enhance T_b . This could be easily achieved by incorporating more metal centres with large spins. Driven by this simple logic, a plethora of polynuclear transition metal complexes with large ground state spins have been synthesized. However, increasing the ground state spin had little or no effect on the energy barrier for magnetization reversal as the ΔE values obtained for large polynuclear structures with giant S are as large as those obtained for structures with much smaller S . The ΔE values of several reported Mn clusters are plotted against their nuclearity in Figure 3 and the resulting plot clearly indicate that the ΔE value of a hexanuclear Mn complex with $S = 12$ is highest among all polynuclear manganese complexes reported so far [13].

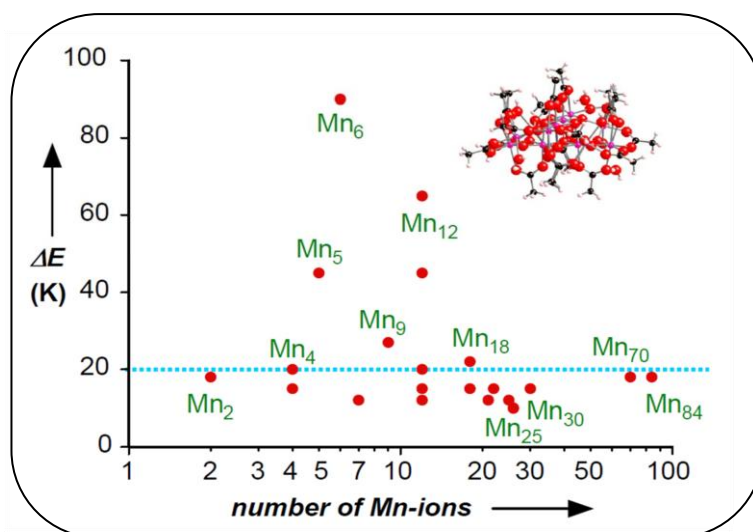


Figure 3. Representative plot of increasing energy against the number of Mn centres.

Therefore, in recent times, efforts to elevate ΔE have been devoted towards enhancing uniaxial anisotropy. Indeed, large uniaxial magnetic anisotropy in lanthanide ions due to strong spin orbit coupling (SOC) has led to observation of slow magnetization reversal even in single ion lanthanide species [14]. More recently, record energy barrier of magnetization reversal has been observed for single ion lanthanide species which can again be attributed to the large uniaxial magnetic anisotropy in such systems [15]. The *f*-orbitals remain essentially degenerate in complexes featuring f-block ions and this leads to large spin-orbit coupling. However, for transition elements, pronounced quenching of the orbital angular momentum is observed owing to the influence of the ligand field. This phenomenon limits the occurrence of significantly large *D* values to a handful of 3d ions for example, Co^{2+} and Mn^{3+} (with octahedral O_h coordination geometry) [16]. To prevent the quenching of the orbital angular momentum in transition metal complexes, the d-orbitals must remain nearly degenerate or lie within a narrow energy gap. This can possibly be achieved if the ligand-field strength is weak. To create such a scenario, the coordination number must be kept low, the coordination environment should be symmetric, and the metal ion should be in a low oxidation state. Another approach which induces reasonable magnetic anisotropy even in high coordinate species is via second order spin-orbit coupling. Contribution to spin-orbit coupling through second order perturbation may occur through spin-orbit interaction of an orbitally non-degenerate ground state with a low lying orbitally degenerate excited state. Thus, even in species with an orbitally non-degenerate electronic ground state, there is a possibility of both inducing and controlling magnetic anisotropy by appropriate manipulation of excited state energy levels. This approach allows the design of magnetically anisotropic building blocks with higher coordination numbers. In spite, of the above, magnetically anisotropic single ion transition metal species which can be used as building blocks for higher nuclearity assemblages are relatively scarce. Moreover, modulation of single ion magnetic anisotropy in molecular species has remained one of the most pressing challenges that need to be overcome for designing high T_b SMMs.

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 pentagonal bipyramidal complexes $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ 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 pentagonal bipyramidal Mn(II) complexes were used as building block to assemble cyano bridged heteronuclear species using different cyanometallates and their magnetostructural correlation was performed.

CHAPTER 1:

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.

CHAPTER 2:

In chapter 2, we have reported the synthesis, characterization, crystal structures and magnetization studies of four pentagonal bipyramidal 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 zero field splitting parameters of **1-4** compounds 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(H₂O) 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 planer pentadentate ligand.

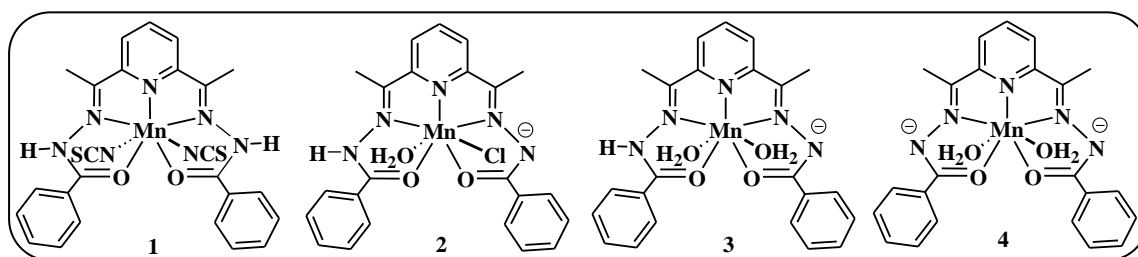


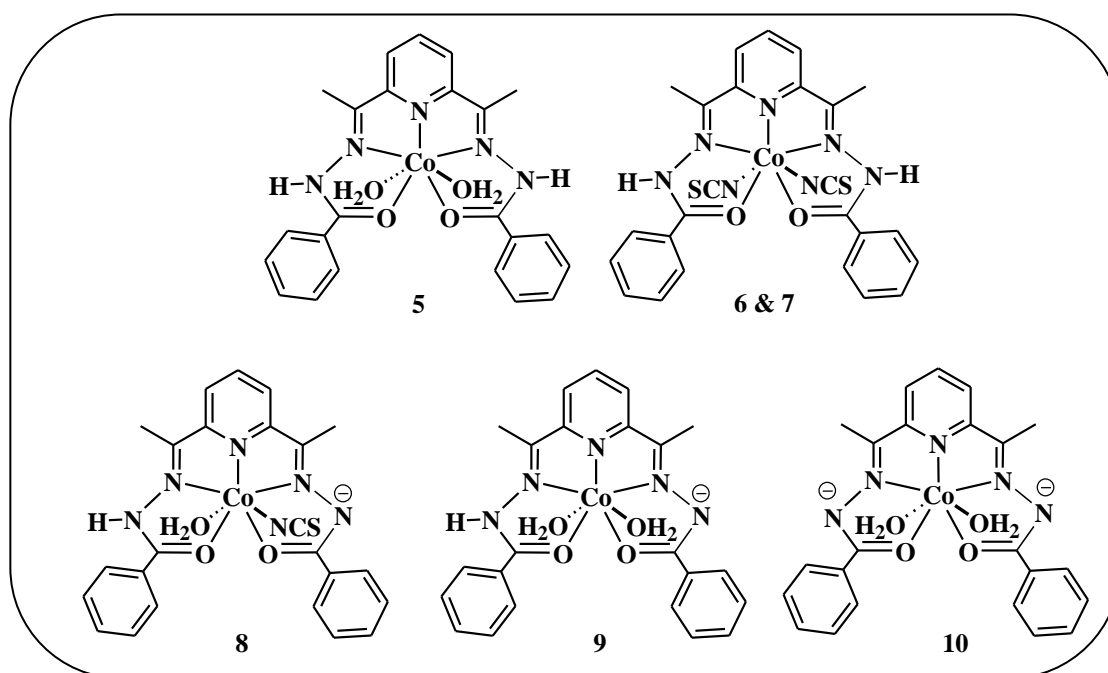
Chart 1. Chemical structures of compounds **1-4**.

The SOD activity of the rigid pentagonal bipyramidal 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 IC₅₀ values are comparable to those observed in case of PBP Mn(II) complexes reported earlier.

CHAPTER 3:

In chapter 3, six pentagonal bipyramidal Co(II) complex of the bis-hydrazone ligand, [Co(H₂L)(H₂O)₂](NO₃)₂.2H₂O (**5**), [Co(H₂L)(SCN)₂].3H₂O (**6**), [Co(H₂L)(SCN)₂].4H₂O (**7**), [Co(HL)(SCN)(H₂O)] (**8**), [Co(HL)(H₂O)₂](NO₃).H₂O (**9**) and [Co(L)(H₂O)₂] (**10**) was prepared and structurally characterized. 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.

The origin of this large positive D parameter in PBP Co(II) complexes lies in spin-orbit coupling 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

Chart 2. Chemical structures of compounds **5-10**

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 spin-orbit coupling 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.

CHAPTER 4:

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. 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 H_2L 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 compounds **13** is in neutral form whereas in compound **14**, it is present in monoanionic form.

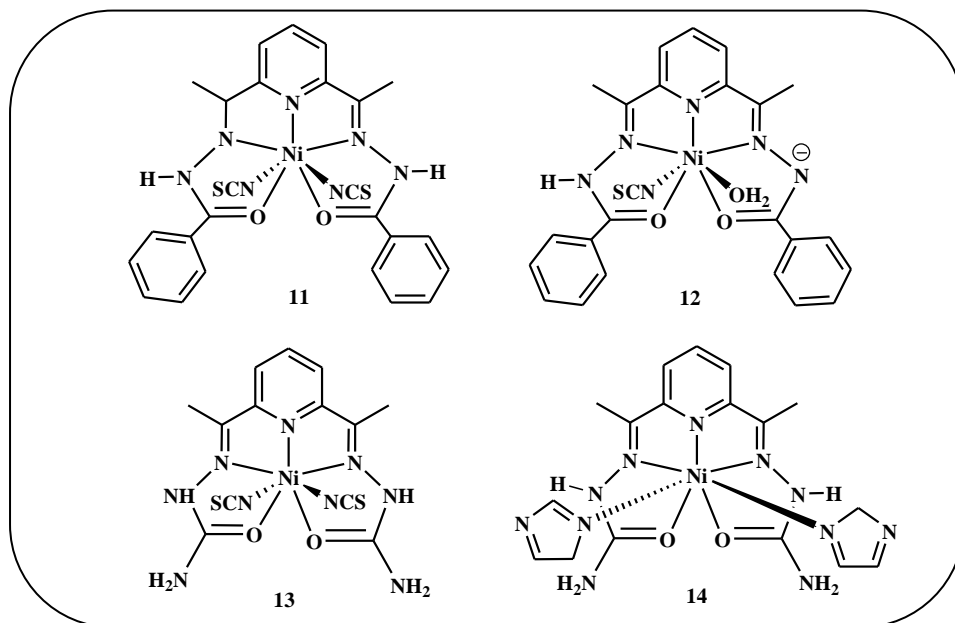


Chart 3. Chemical structures of compounds **11-14**

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

CHAPTER 5:

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, $[\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ with the cyanometallate linkers having different charge, e.g. $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$. Results presented herein show that intricate control over the self-assembly process can also be achieved by proper choice of reaction medium. Reaction of $[\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ with $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ 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 $[\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})\text{Cl}]\text{Cl}$ with $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ in the presence of KSCN.

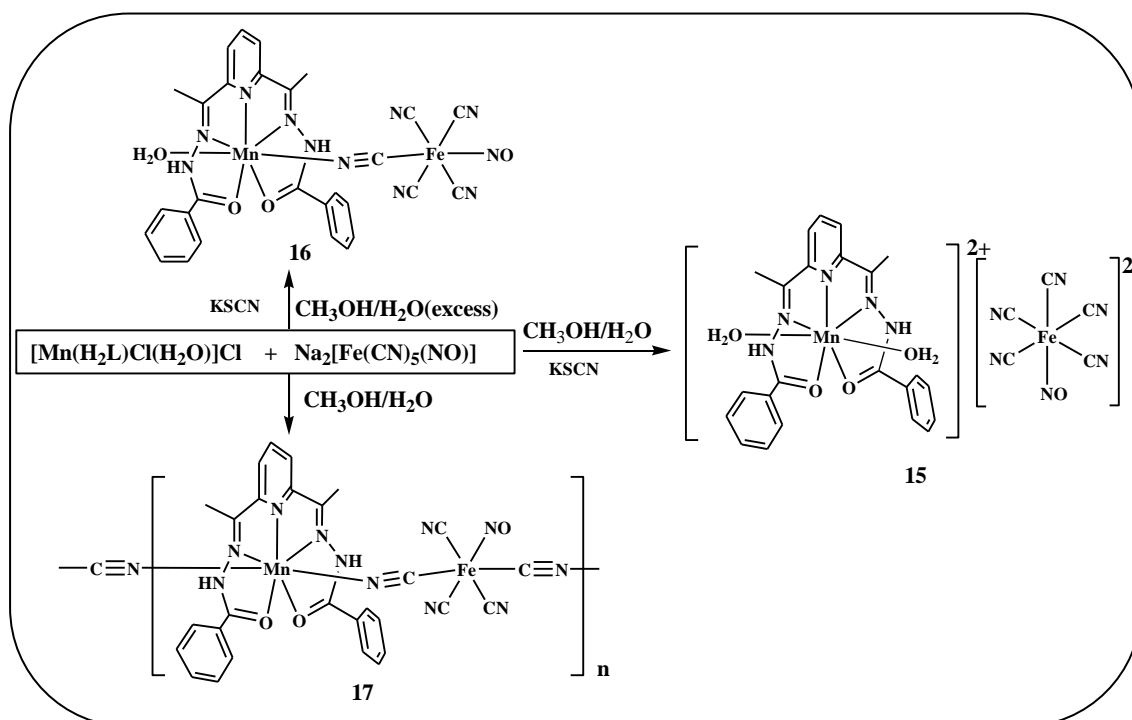


Chart 4. Chemical structures of compounds **15-17**

Presence of KSCN hindered the coordination of cyanometallate with the PBP Mn(II) and simple binuclear salt, $[\text{Mn}(\text{H}_2\text{L})(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_5(\text{NO})]\cdot\text{H}_2\text{O}$ (**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 $[\{\text{Mn}(\text{H}_2\text{L})\}\{\text{Fe}(\text{CN})_5(\text{NO})\}]$ (**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.

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, $[\{\text{Mn}(\text{L})(\text{H}_2\text{O})\}_2\{\text{Mn}(\text{L})\}\{\text{Fe}(\text{CN})_6\}_2]\cdot 9\text{H}_2\text{O}$ (**18**) and $[\text{Mn}(\text{L})(\text{H}_2\text{O})_2]_2[\{\text{Mn}(\text{L})(\text{H}_2\text{O})\}_2\{\text{Fe}(\text{CN})_6\}][\{\text{Mn}(\text{L})\}_2\{\text{Fe}(\text{CN})_6\}_3]\cdot 13\text{H}_2\text{O}$ (**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 **18** is quite prevalent, while the structure of nonanuclear compound **19** is unique due to the presence of four isolated motifs. 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 association of cyanometallates in a predetermined fashion will allow us to explore the potential of these species in building molecular magnets with better characteristics.

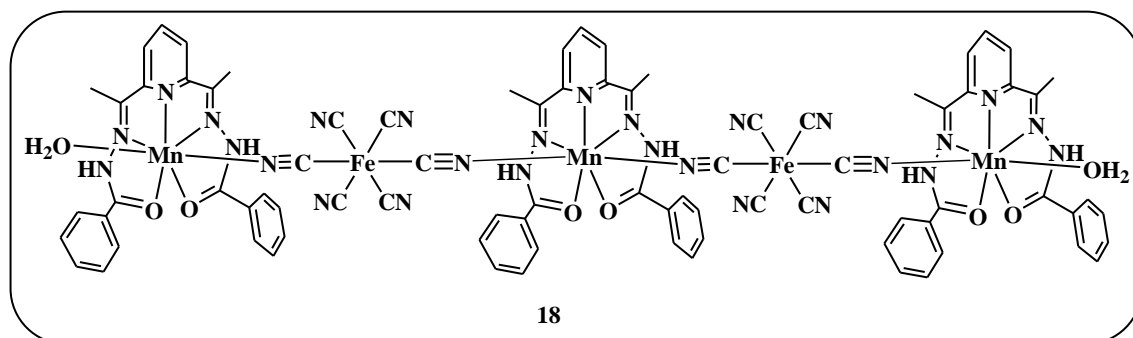


Chart 5. Chemical structure of compound **18**

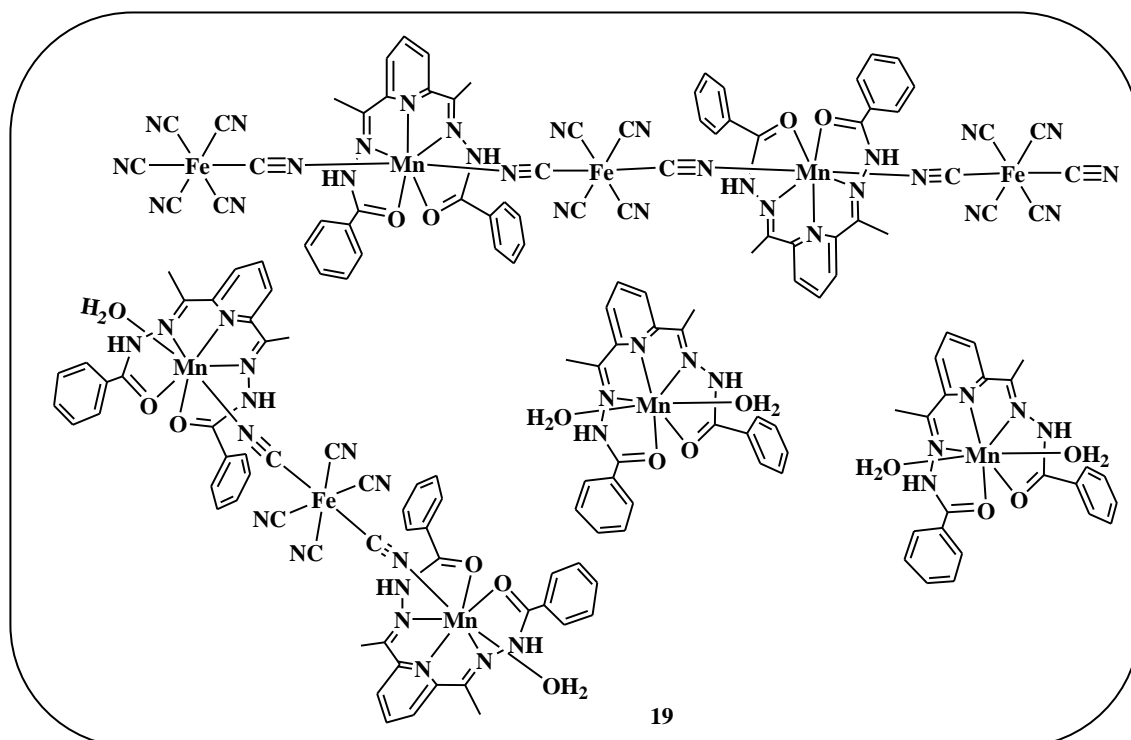


Chart 6. Chemical structure of compound 19

CHAPTER 6:

Finally, chapter 6 summarized the results discussed in the above chapters 2-5, providing the correlation of the coordination environment and magnetic anisotropy in heptacoordinated PBP compounds of Mn(II), Co(II) and Ni(II). Based on the salient features of the entire thesis work, future prospects and outlook to improve and consolidate the research work will also be presented in this chapter.

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