

Chapter 1

A General Introduction on Magnetic Anisotropy of Two- to Seven-Coordinate Complexes

1.1. General Introduction

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 magnetization along all 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 thereby devise rational routes to manipulate it in a premeditated or predetermined fashion. The prime underlying cause of magnetic anisotropy is zero field splitting (ZFS), which lifts degeneracy of the M_s levels even in the absence of any external magnetic field bias. For example, in case of $S = 3/2$ system, degeneracy of spin states can be removed by ZFS in two different ways as shown in Figure 1.1.

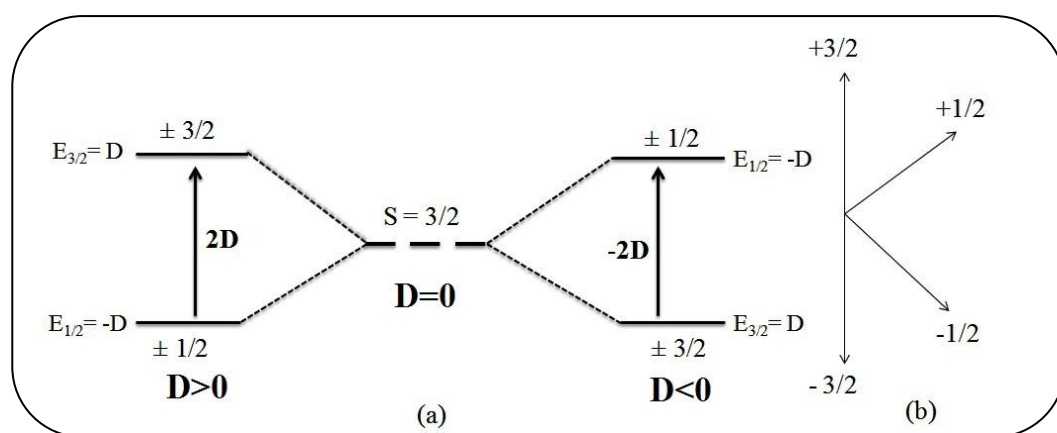


Figure 1.1. (a) Splitting of M_s levels for a $S = 3/2$ system in absence and presence of ZFS (b) Orientation of M_s levels for $S = 3/2$ system in presence of external magnetic field

The Hamiltonian for axial ZFS is given by the expression:

$$\hat{H} = D[S_z^2 - S(S+1)/3]$$

where, D is the axial ZFS parameter, S is the ground spin state and S_z is the component of spin in the z -direction. Thus, the difference in energy between the M_s levels after ZFS can be easily calculated. From the Figure 1.1, it is evident that a negative difference in energy between the excited M_s levels signifies the stabilization of the highest M_s level. Thus, due to negative axial ZFS parameter, the population in $M_s = \pm 3/2$ state increases even without application of any external magnetic field and therefore, the system possesses an easy axis of magnetization (along $M_s = \pm 3/2$ in this case). Similarly, a positive difference in energy indicates the stabilization of the lowest M_s state ($M_s = \pm 1/2$ for $S = 3/2$ system). Thus, the population in $M_s = \pm 1/2$ state increases and it is easier to magnetize it along $M_s = \pm 1/2$ direction (easy plane of magnetization).

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 tunneling 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

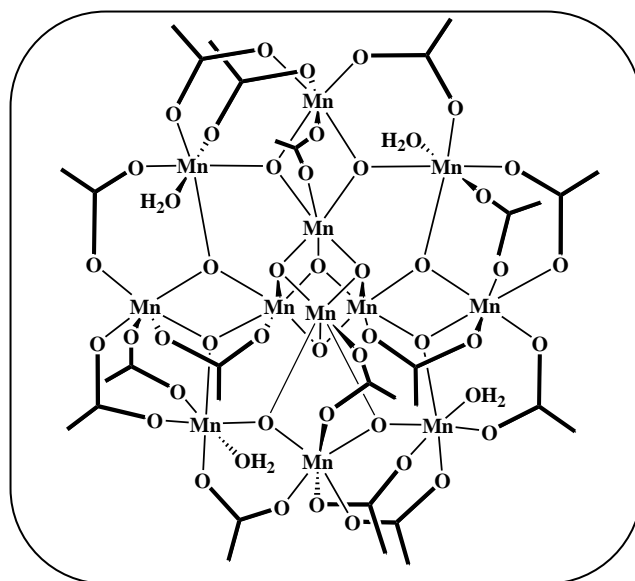


Figure 1.2. Structure of $[\text{Mn}_{12}\text{O}_{12}(\text{COOCH}_3)_{16}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (Mn_{12})

temperature called blocking temperature (T_b) and are termed as Single Molecule Magnets (SMMs) [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}) (Figure 1.2) [10]. When a sample of the Mn_{12} complex was kept below temperature T_b , the slow relaxation of magnetization was observed even after the removal of the external magnetic field. During the past two decades, the field of SMMs has grown dramatically and extensive research has led to many wonderful discoveries of new technologies [10-11]. SMMs are of great importance in today's scenario, not only because of their size, but also for their intriguing properties such as:

- a) Each molecule behaves as a magnet, so the extent of magnetization is much more than classical bar magnets.
- b) Due to the presence of organic substituents attached, SMMs have low densities as compared to conventional magnets.
- c) Better solubility in common organic solvents, as compared to conventional magnets.
- d) Magnetic properties of SMMs can be tuned by means of simple organic chemistry.
- e) Better biocompatibility and compatibility with polymers for composites.
- f) SMMs offer the possibility to design transparent magnets.
- g) SMMs cause low environmental contamination.
- h) Through proper choice of organic substituents, multifunctional magnets can be assembled.

Molecular magnetism is now an emerging area in many disciplines, such as material science, molecular dynamics, information technology, etc. mainly due to their property of reproducibility and multifunctionality of their building blocks. The application of magnetic materials in information storage technology depends on their ability to remain in the magnetized state for long time. Small magnetic particles cannot keep their spins aligned for a longer time, and they slowly relax from one state to the other, thereby, losing their capacity of storing information [12-13]. Therefore, tremendous efforts are currently devoted towards development of molecular species which show slow relaxation of magnetization at higher temperature.

The magnetization and slow magnetic relaxation in SMMs can be described well with the help of a double well potential energy diagram. Variable field magnetization and high field electron paramagnetic resonance (HFEPR) indicate that the neutral ferromagnetic dodecanuclear Mn_{12} complex has an integral spin of $S=10$ ground state. The antiferromagnetic coupling between $S=3/2$ spins of Mn^{IV} and $S=2$ spin of Mn^{III} ions leads to $S=10$ ground state and it splits into 21 ($M_s = +10$ to $M_s = -10$) microstates due to ZFS (Figure 1.3) [14]. 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 down) level will be more populated compared to the $M_s = +10$ (spin up) level. 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 ZFS 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 [13].

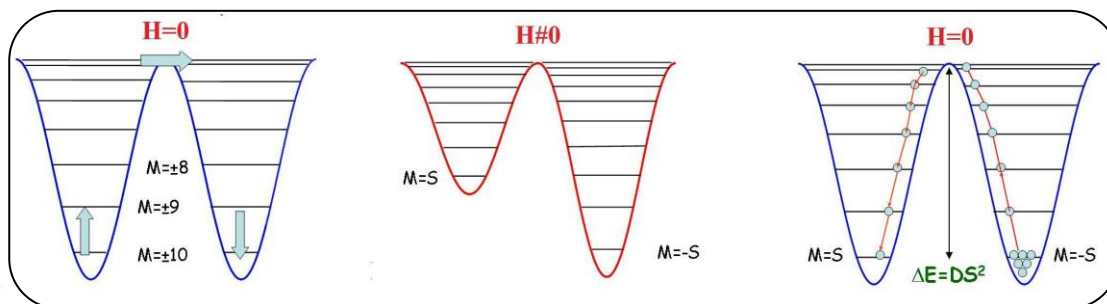


Figure 1.3. Double well potential energy diagram of Mn_{12} complex in the absence of magnetic field, on application of a magnetic field and on removal of the magnetic field again

Further, the energy barrier for magnetization reversal is given by the expression $\Delta E = -DS^2$. For Mn_{12} complex, $\Delta E = 50 \text{ cm}^{-1}$ but at 300 K, $KT = 208 \text{ cm}^{-1}$ ($K = 0.695 \text{ cm}^{-1}/\text{K}$) and therefore spontaneous relaxation of magnetization is observed at room temperature. However, if the temperature of the system is kept below 4 K, 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 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 1.4 and the resulting plot clearly indicate that the ΔE value of a hexanuclear Mn complex with $S = 12$ is highest among all polynuclear Mn complexes reported so far [13].

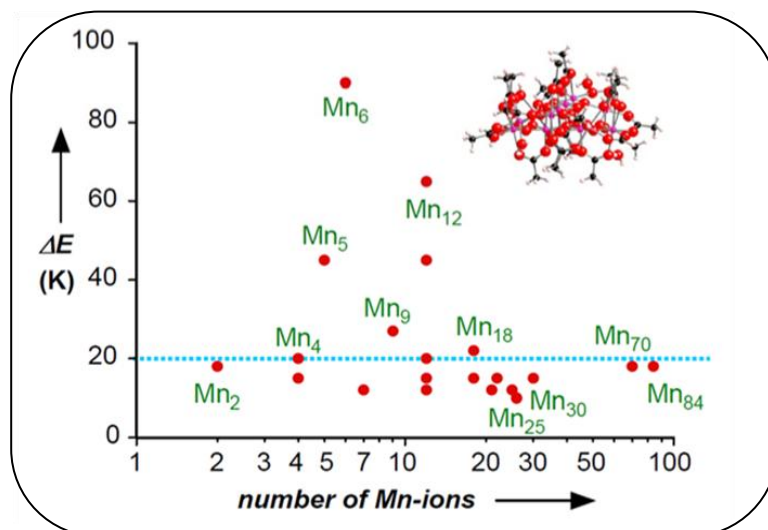


Figure 1.4. Representative plot of increasing energy against the number of Mn centres

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]. Lanthanide complexes possess large

uniaxial anisotropy originating from SOC and thus many of these complexes show large energy barrier for magnetization reversal [15-17]. The energy barrier for the double-decker lanthanide complex, $[\text{Tb}(\text{Pc})_2]^-$ (**I**) (Pc: phthalocyanine dianion) has been reported to be 584 cm^{-1} , followed by $[\{\text{Pc}(\text{OEt})_8\}_2\text{Tb}]^+$ (**II**) ($U_{\text{eff}} = 550 \text{ cm}^{-1}$) and $[\{\text{Pc}(\text{OEt})_8\}_2\text{Tb}]^+$ (**III**) ($U_{\text{eff}} = 509 \text{ cm}^{-1}$) [18-19]. More recently, unprecedented high energy barrier of magnetization reversal has been observed in several single ion lanthanide species which can again be attributed to the large uniaxial magnetic anisotropy in such systems [20].

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, e.g. Co^{2+} and Mn^{3+} (with octahedral O_h coordination geometry) [21]. 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. Recent studies have established that in low coordinate 3d complexes with a symmetric and weak ligand environment, quenching of orbital angular momentum is significantly reduced as the d-orbitals lie within a narrow energy gap. For example, due to large uniaxial anisotropy in mononuclear two coordinate Fe(I) complex, $[\text{K}(\text{crypt-222})][\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]$ (**IV**), record energy barrier of 226 cm^{-1} for magnetization reversal has been observed (Figure 1.5) [22-23]. Due to the two-coordinate geometry and low oxidation state of the metal ion, orbital angular momentum remains almost unquenched. This eventually leads to a large SOC constant and a simultaneous rise in energy barrier for magnetization reversal is observed.

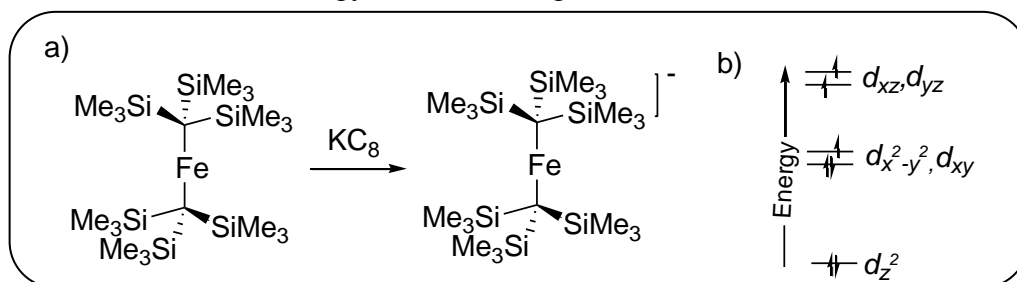


Figure 1.5. a) Scheme showing reduction of $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]$ (**IV**) using KC_8 ; b) d-orbital splitting pattern in $[\text{Fe}(\text{C}(\text{SiMe}_3)_3)_2]^-$

However, low coordinate species are chemically stable only under inert atmosphere and this severely limits their possible utility in different applications. In this context, an approach to induce magnetic anisotropy in high coordinate transition metal species is highly desirable. An appealing approach which induces reasonable magnetic anisotropy even in high coordinate species is via second order SOC. Contribution to SOC 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. Increasing magnetic anisotropy by adopting unconventional coordination geometry has emerged as a promising strategy for enhancing energy barrier for magnetization reversal in SMMs [24-27]. 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. In view of this, efforts to rationally manipulate the magnetic anisotropy of molecular species have intensified during the last few years [28-29]. However, parameters governing magnetic anisotropy are poorly understood and intricate control over magnetic anisotropy has remained one of the most formidable challenges. So, a systematic literature survey on the dependence of magnetic anisotropy on the coordination geometry and environment of the two- to seven-coordinate complexes reported so far has been carried out to identify underlying parameters which govern magnetic anisotropy.

1.2. Magnetic anisotropy in two-coordinate complexes

Two-coordinate complexes of d^1 - d^9 ions are very rare and are least investigated because they tend to undergo aggregation and are highly susceptible to react with air or moisture. Many attempts were made in recent times by various groups to avoid the aggregation by attaching sterically bulk ligands, so that they can be isolated in ambient temperature. Despite this shortcoming, two coordinate complexes are gaining much attention these days due to their fascinating magnetic properties. Several 3d transition metal complexes with coordinatively unsaturated two coordinate geometries have been

reported. Two-coordinate complexes can either possess linear (D_h) or non-linear (C_{2v}) geometry. The energy sequences of d-orbitals in linear and bent two-coordinate complexes are shown in Figure 1.6. From the d-orbital energy sequence in linear two coordinate transition metal complexes, existence of unquenched orbital momentum can be anticipated in high spin d^1 , d^3 , d^6 and d^8 configurations. However, among these, stable two-coordinate complexes are known for d^6 and d^8 configurations only. While all the reported d^8 two-coordinate complexes have shown negligible orbital magnetic moment, in case of two-coordinate d^6 complexes, large unquenched orbital magnetic moment is observed.

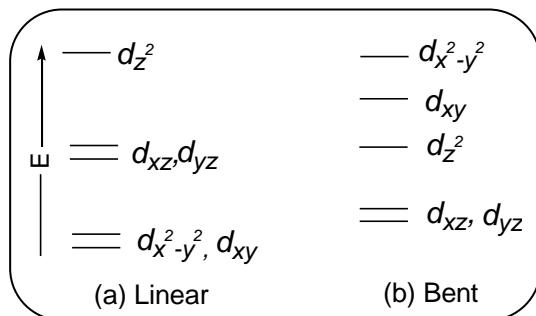


Figure 1.6. Energy level sequences of d-orbitals in two-coordinate complexes in (a) linear D_{oh} and C_{ov} geometries and (b) bent C_{2v} geometry

The first examples of two-coordinated complexes $[M\{N(SiMePh_2)_2\}]$ [$M=Fe$ (**V**), Co (**VI**)] were reported by Bartlett and Power in 1987 [30]. Magnetization measurements revealed that the magnetic moments of complexes **V** and **VI** are close to those expected for free $Fe(II)$ and $Co(II)$ ions respectively [31]. Apart from that, large internal hyperfine fields ($H_{int} = 152$ T) observed in low temperature Mössbauer spectra of rigorously linear, homoleptic, two-coordinate Fe^{II} complex, $[Fe\{C(SiMe_3)_3\}_2]$ (**VII**) initially demonstrated the presence of unquenched orbital angular momentum in such species [32]. Considering negligible SOC, the high spin d^6 complex **VII** shall have a degenerate Δ_g electronic ground state (in D_{oh} symmetry) in which three electrons occupy the degenerate $d_{x^2-y^2}$ and d_{xy} orbitals. Thus, an electron can move between the degenerate $d_{x^2-y^2}$ and d_{xy} without spin reversal and orbital angular momentum along the axis (the C_3 axis along z-direction which interconverts these orbitals) shall remain unquenched. In general, molecules featuring degenerate ground states undergo Jahn-

Teller distortion to lower the symmetry and thus remove the degeneracy. However, for linear molecules, Jahn-Teller distortion cannot occur and thus the ground state degeneracy in complex **VII** is retained. Consequently, orbital angular momentum remains largely unquenched and virtual free ion magnetic character is observed in complex **VII** (Chart 1.1) [32].

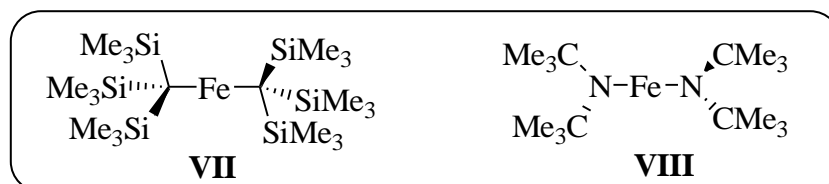


Chart 1.1. Structure of $[\text{Fe}\{\text{C}(\text{SiMe}_3)_3\}_2]$ (**VII**) and $[\text{Fe}\{\text{N}(t\text{-Bu})_2\}_2]$ (**VIII**)

Girolami and co-workers reported another example of homoleptic two-coordinate Fe(II) complex, $[\text{Fe}\{\text{N}(t\text{-Bu})_2\}_2]$ (**VIII**) with an almost linear geometry (Chart 1.1) [33]. As in case of complex **VII**, large first order contribution to orbital angular momentum is present in this complex also, due to degenerate electronic ground state. However, the internal hyperfine field ($H_{\text{int}} = 105$ T) is weaker as compared to $[\text{Fe}\{\text{C}(\text{SiMe}_3)_3\}_2]$ (**VII**) which can be attributed to significant spin-orbit state mixing enabled by lower symmetry in $[\text{Fe}\{\text{N}(t\text{-Bu})_2\}_2]$ (**VIII**).

Dynamic susceptibility studies reported by Long and co-workers, on a series of linear two-coordinate Fe(II) complexes, $[\text{Fe}\{\text{N}(\text{SiMe}_3)(\text{Dipp})\}_2]$ (**IX**), $[\text{Fe}\{\text{C}(\text{SiMe}_3)_3\}_2]$ (**X**), $[\text{Fe}\{\text{N}(\text{H})\text{Ar}'\}_2]$ (**XI**), $[\text{Fe}\{\text{N}(\text{H})\text{Ar}^*\}_2]$ (**XII**) and $[\text{Fe}(\text{OAr}')_2]$ (**XIII**) (Dipp: $\text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$; Ar' : $\text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-Pr}^i_2)_2$; Ar^* : $\text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Pr}^i_2)_2$) established that the large uniaxial anisotropy originating from unquenched orbital angular momentum effectively increases the energy barrier for magnetization reversal in these complexes [34]. For $[\text{Fe}\{\text{N}(\text{SiMe}_3)(\text{Ar})\}_2]$ (**XIV**), (Ar : diisopropylphenyl), the measured U_{eff} (181 cm^{-1}) is several folds higher as compared to the prototypical SMM Mn_{12} ($U_{\text{eff}} = 46$ cm^{-1}). Therefore, one would normally expect to observe slow relaxation of magnetization at elevated temperatures. Surprisingly, none of the reported two-coordinate Fe(II) complexes displays slow relaxation of magnetization in the absence of an external field bias. This could primarily be attributed to quantum tunneling of magnetization (QTM), which allows quick relaxation of spins without ascending the thermal activation energy barrier for spin reversal. The origin of QTM can be attributed to the efficient mixing of

ground $\pm M_s$ levels, due to the presence of transverse ZFS (E). The applied field bias lifts the degeneracy of $\pm M_s$ levels and thereby suppresses QTM.

It has been mentioned earlier that due to the two-coordinate geometry and low oxidation state of the metal ion, the orbital angular momentum in [K(crypt-222)] [Fe^I(C(SiMe₃)₃)₂] (**XV**) remains almost unquenched (Figure 1.4) [35]. This eventually leads to large spin orbit coupling, and a simultaneous rise of the energy barrier for magnetization reversal is observed. The measured $U_{\text{eff}} = 226 \text{ cm}^{-1}$ is unprecedentedly large among transition metal species. More than a decade ago, Klatyk and coworkers recognized the existence of unquenched orbital angular momentum for a Fe(I) ion in a weak axial coordination environment [36]. This investigation was performed on the iron nitridometallate, Li₂[(Li_{1-x}Fe^I_x)N] where Fe(I) is doped within an alkali metal nitride host matrix. Intriguingly, for [Fe(C(SiMe₃)₃)₂]⁻ and Li₂[(Li_{1-x}Fe^I_x)N], computational studies establish that efficient mixing of 3d_{z²} and 4s orbitals stabilizes the 3d_{z²} orbital. Thus, the d-orbital energy level sequence in [Fe(C(SiMe₃)₃)₂]⁻ (**IV**) (or Li₂[(Li_{1-x}Fe^I_x)N]) does not follow the conventional trend expected for a linear two-coordinate complex and accounts for the presence of unquenched orbital angular momentum as shown in Figure 1.4.

Power reported two-coordinate Fe^{II} complex, [Fe{N(H)Ar[#]}₂] (**XVI**), Ar[#] = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂ in linear and bent geometry (Chart 1.2). It is pertinent to note here that large quenching of orbital angular momentum is observed in bent two-coordinate Fe(II) complex compared to the almost free ion magnetism observed for linear counterpart. The electronic degeneracy is lifted (Δ_g in $D_{\text{oh}} \rightarrow A_1 + A_2$ in C_{2v}) due to the

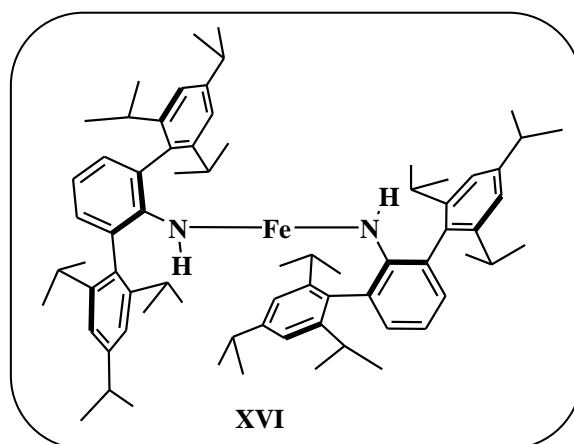


Chart 1.2. Structure of linear [Fe{N(H)Ar[#]}₂] (**XVI**)

bent geometry of complex **XVI** [37]. Consequently, significant quenching of orbital angular momentum is effected as the two orbitals are no longer interconvertible by a symmetry operation in the C_{2v} point group.

Several two-coordinate Co(II) complexes have been reported in recent times and their magnetic properties are also investigated. Power and coworkers reported a linear $[Co(OAr^{Me}_6)_2]$ (**XVII**) $\{Ar^{Me}_6: C_6H_3-2,6(C_6H_2-2,4,6-Me_3)_2\}$ and both linear and bent form of $[Co(OAr^{iPr}_4)_2]$ (**XVIII**) $\{Ar^{iPr}_4: C_6H_3-2,6(C_6H_2-2,4,6-Pr^i_2)_2\}$ (Chart 1.3) [38]. Further, they have reported almost linear two coordinate Co(II) complex, $[CoAr'_2]$ (**XIX**) and a bent complex, $[Ar'CoN(SiMe_3)_2]$ (**XX**) $\{Ar': C_6H_3-2,6-(C_6H_3-2,6-^iPr_2)_2\}$ [39]. The observed magnetic moment ($\mu_{eff} = 5.65$ BM) of the linear complex **XVIII** is unusually large as compared to the spin only moment ($\mu_{spin\ only} = 3.87$ BM) which indicate significant orbital contribution. Conventional energy sequence of the d-orbitals for an high spin d^7 ion in linear two-coordinate geometry predicts an electronic configuration $(d_x^2-y^2, d_{xy})^4(d_{xz}, d_{yz})^2(d_z^2)^1$, where no first order orbital contribution is present. The authors attributed the observed large moment to the presence of second order orbital contribution resulting from spin-orbit mixing of the electronic states. However, detailed computational analysis of d^7 ion in linear two-coordinate geometry have predicted a completely different d-orbital energy sequence due to the efficient mixing of $3d_z^2$ and $4s$ as shown previously (Figure 1.5). The interplay of similar mixing of orbitals in case of the above linear Co(II) complex has been inferred and this could possibly account for the large orbital contribution to effective magnetic moment.

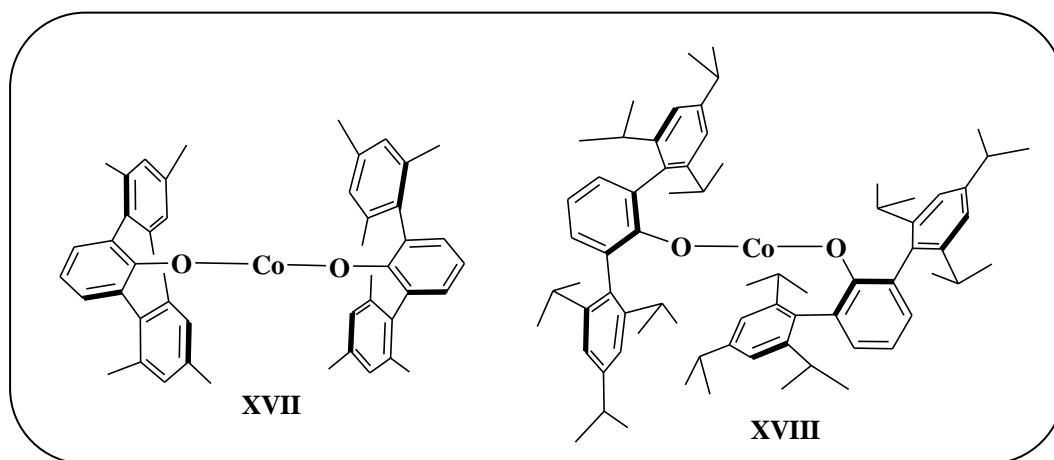


Chart 1.3. Structures of $[Co(OAr^{Me}_6)_2]$ (**XVII**) and $[Co(OAr^{iPr}_4)_2]$ (**XVIII**)

Again in 2014, Power and coworkers reported three salts of two-coordinate Fe(I), Co(I) and Ni(I) complexes, $[\text{K}(\text{Et}_2\text{O})_2(18\text{-crown-6})][\text{Fe}\{\text{N}(\text{SiMe}_3)\text{Dipp}\}_2]$ (**XXI**) and $[\text{K}(18\text{-crown-6})][\text{M}\{\text{N}(\text{SiMe}_3)\text{Dipp}\}_2]$ {M= Co (**XXII**) and Ni (**XXIII**)} (Chart 1.4) [40]. Magnetization studies on the polycrystalline samples of these complexes reveals that the Fe(I) and Co(I) complexes, **XXI** and **XXII** possess large orbital contribution to their magnetic moments with $D = -65 \text{ cm}^{-1}$ (**XXI**) and -183 cm^{-1} (**XXII**) respectively, whereas the Ni(I) complex **XXIII** has negligible D value.

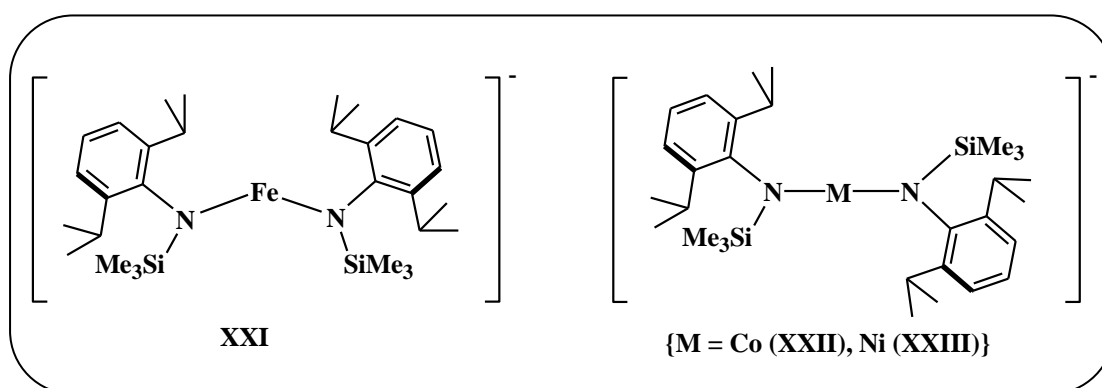


Chart 1.4. Structures of compounds **XXI** (left), **XXII** and **XXIII** (right)

Murugesu and coworkers have successfully synthesized and characterized a very rare example of a two-coordinate N-heterocyclic carbene based Ni(I) complex, $[\text{Ni}(6\text{-Mes})_2]\text{Br}$ (**XXIV**) (Chart 1.5) [41]. Complex **XXIV** has been found to be almost linear with C-Ni-C bond angle of 177.7° . Magnetic susceptibility measurements of this complex revealed that it is the first example of mononuclear Ni(I) complex which shows field induced slow relaxation of magnetization with U_{eff} of 17 K.

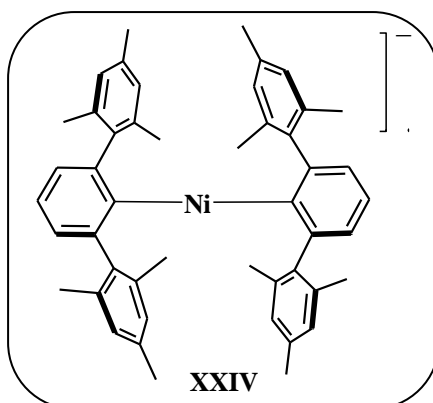


Chart 1.5. Structure of the Ni(I) cation in $[\text{Ni}(6\text{-Mes})_2]\text{Br}$ (**XXIV**)

Thus, the above examples establish that two-coordinate geometries are highly preferred choice for developing species with large magnetic anisotropy. As described above, the low coordination number keeps the d-orbitals more or less degenerate and Jahn-Teller distortion also does not occur in linear two-coordinate complexes. Therefore, record breaking energy barrier for magnetization reversal are observed in several two-coordinate complexes. However, the lack of stability due to coordination unsaturation has severely limited studies as well as application of two coordinate species and very few examples as described above have been reported so far.

1.3. Magnetic anisotropy in three-coordinate complexes

Three-coordinate complexes are electronically unsaturated with less number of valence electrons (less than 18) and therefore such complexes are also less frequently studied. Three-coordinate complexes show either trigonal planar (D_{3h}) or trigonal pyramidal (C_{3v}) geometry and the splitting pattern of d-orbitals in these geometries have been depicted in Figure 1.7. In general, d^1 , d^6 , d^4 and d^9 ions in trigonal planar geometry are expected to show strong orbital angular momentum with a large negative D value, whereas d^2 and d^7 complexes exhibit large positive D values.

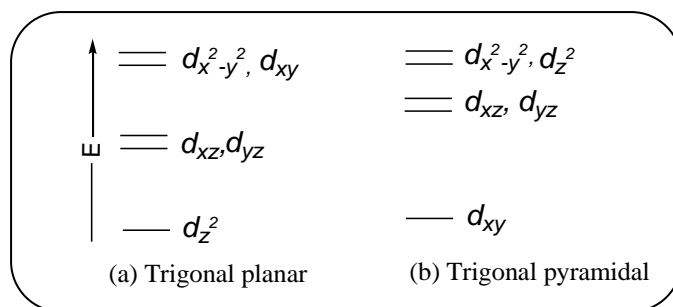


Figure 1.7. Energy level sequences of d-orbitals in three-coordinate complexes in (a) trigonal planar (D_{3h}) geometry and (b) trigonal pyramidal (C_{3v}) geometry

The D values of several three-coordinate mononuclear complexes reported so far are listed in Table 1.1. It is pertinent to note here that three-coordinate Co(II) complexes exhibit large negative value of D in the range of -57 to -82 cm^{-1} . However, axial ZFS parameters of the three-coordinate mononuclear Fe(II) complexes generally lies within the range -7.6 to -25.1 cm^{-1} and reasonably lower as compared to Co(II) complexes. The ZFS parameter ($D = + 20.4$ cm^{-1}) of only one trigonal planar Fe(I) complex,

[FeCl(cAAC)₂] (**XXXVIII**) prepared by using a cyclic alkyl(amino) carbene (cAAC) has been reported so far [42]. Some of the interesting studies on ZFS parameters of three-coordinate complexes reported so far are described below.

Table 1.1. Reported D value of few three-coordinate mononuclear complexes.

Sl. No.	Complex	D (cm ⁻¹)	References
1.	[Fe(N(SiMe ₃) ₂) ₂ (PCy ₃)] (XXVI)	-33	43
2.	[Fe(N(SiMe ₃) ₂) ₂ (THF)] (XXVII)	-20	44
3.	[Li(15-crown-5)][Fe(N(SiMe ₃) ₂) ₃] (XXVIII)	9.9	44
4.	[Li(15-crown-5)][Co(N(SiMe ₃) ₂) ₃] (XXIX)	-57	44
5.	[Na(15-crown-5)][Co(N(SiMe ₃) ₂) ₃] (XXX)	-62	44
6.	[Co(N(SiMe ₃) ₂)(THF)] (XXXI)	-72	44
7.	[Co(N(SiMe ₃) ₂)(pyridine)] (XXXII)	-82	45
8.	[Co(N(SiMe ₃) ₂)(PCy ₃)] (XXXIII)	-82	44
9.	[Co(N(SiMe ₃) ₂)(PMe ₃)] (XXXIV)	-74	45
10.	[Fe(N(SiMe ₃) ₂) ₂ (ⁱ Pr)] (XXXV)	-18.2	46
11.	[Fe(N(SiMe ₃) ₂) ₂ (ⁱ Mes)] (XXXVI)	-23.3	46
12.	[Fe(H ₂ B(^t BuIm) ₂) ₂] (XXXVII)	-25.1	46
13.	[FeCl(cAAC) ₂] (XXXVIII)	20.4	42

^tBuIm: bis(3-tert-butyl-imidazol-2-ylidene)borate; cAAC : cyclic alkyl(amino) carbene;

ⁱMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene; ⁱPr : isopropyl; THF: Tetrahydrofuran

Andres and coworkers recently reported a series of trigonal planar Fe(II) complexes, [Fe^{II}LX] (**XXV**) {X: Cl⁻, CH₃⁻, NHTol⁻, NH^tBu⁻ and L₃: N,N'-bis(2,6-diisopropylphenyl)-2,2,6,6-tetramethylheptane-3,5-di-iminato-N,N' or β-diketimate} supported by bulky β-diketimate ligand (Chart 1.6) [47]. Low temperature Mössbauer spectrum of these complexes showed internal hyperfine fields of large magnitudes originating from unquenched orbital angular momentum. Due to the distorted trigonal planar geometry in these complexes, the realistic d-orbital energy sequence deviate from that of idealized energy diagram. As shown in Figure 1.7, the d_{yz} and d_{z²} orbital are closely spaced and this eventually leads to an out-of-state (non-degenerate state)

SOC. Intriguingly, as the difference in energy between the d_{yz} and d_z^2 orbitals are varied, the magnitude of out-of-state SOC also changes which in turn can be attributed to the difference in internal hyperfine fields in the above series of three-coordinate Fe(II) complexes.

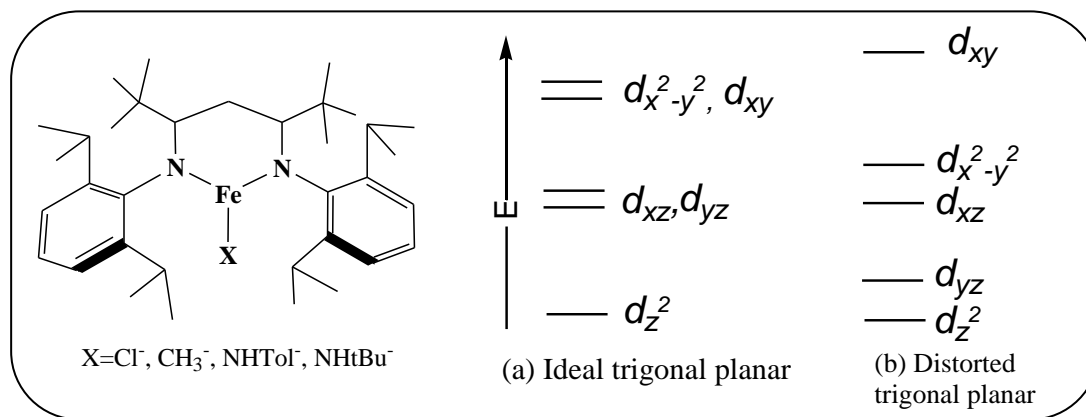


Chart 1.6. Molecular structure of [Fe(II)LX] (**XXV**) in trigonal planar geometry and splitting pattern of d-orbitals in (a) ideal and (b) distorted trigonal planar geometry

Murugesu and coworkers have reported dynamic susceptibility studies on a planar three-coordinate Fe(II) complex, [Fe(N(SiMe₃)₂)₂(PCy₃)] (**XXVI**) (Cy: cyclohexyl) (Chart 1.7) [43]. The complex **XXVI** undergoes slow relaxation of magnetization under an applied dc field due to the presence of uniaxial magnetic anisotropy with $D = -7.6 \text{ cm}^{-1}$ and the effective energy barrier for magnetization reversal, U_{eff} was found to be 29 cm^{-1} . The ground electronic state of the complex is non-degenerate as described in case of the earlier described trigonal planar Fe(II) complexes. However, intermingling of the

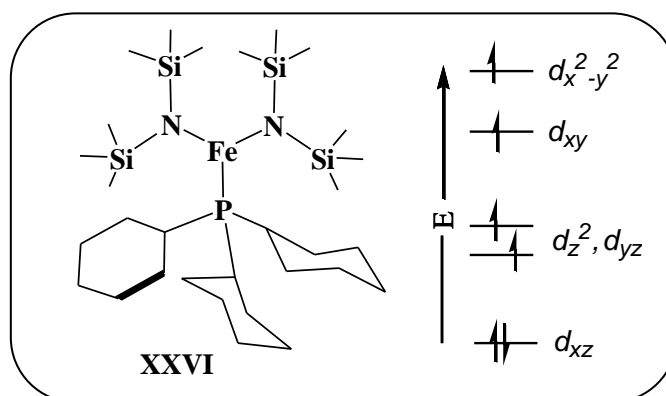


Chart 1.7. Molecular structure of [Fe^{II}(N(TMS)₂)₂(PCy₃)] (**XXVI**) and its d-orbital splitting pattern

low-lying electronic excited states with the ground electronic state of high spin Fe(II) ion leads to reintroduction of orbital angular momentum into the ground electronic state. Power and coworkers investigated the axial ZFS parameters of a series of monomeric three coordinated Co(II) complexes, [Co(N(SiMe₃)₂)(THF)] (**XXXI**), [Co(N(SiMe₃)₂)(pyridine)] (**XXXII**), [Co(N(SiMe₃)₂)(PCy₃)] (**XXXIII**), [Co(N(SiMe₃)₂)(PMe₃)] (**XXXIV**) and [Na(15-crown-5)][Co(N(SiMe₃)₂)₃] (**XXX**) and the D values of these species are found to be large negative ranging between -62 cm⁻¹ to -82 cm⁻¹ [45]. Subsequent studies reported by Eichhöfer and coworkers revealed that monomeric three coordinated Co(II) complexes undergo slow relaxation of magnetization under applied dc field due to the presence of large negative ZFS parameter [44]. Similar studies carried out on three coordinate Fe(II) complexes revealed that apart from [Fe(N(SiMe₃)₂)₂(PCy₃)] (**XXVI**), other reported Fe(II) species e.g. [Fe(N(SiMe₃)₂)(THF)] (**XXVII**) and [Li(15-crown-5)][Fe(N(SiMe₃)₂)₃] (**XXVIII**) do not show slow relaxation of magnetization and the D parameters of these complexes are reported to be -33, -20 and +9.9 cm⁻¹ respectively [44]. Theoretical calculations revealed that deviation from strictly ideal trigonal planar environment removes the orbital degeneracy of the d_{xz} & d_{yz} and d_{x²-y²} & d_{xy} orbitals. This essentially lowers the energy of excited states involved in SOC and therefore in case of [Fe(N(SiMe₃)₂)₂(PCy₃)] (**XXVI**) and [Fe(N(SiMe₃)₂)(THF)] (**XXVII**) the D parameters are negative. Moreover, π-acceptor ligands like PCy₃ lowers the energy of d_{xz} orbital and therefore the out-of-state SOC is more pronounced in case of [Fe(N(SiMe₃)₂)₂(PCy₃)] (**XXVI**) which eventually leads to a large negative D value and slow relaxation of magnetization in this case. A similar trend is also observed in case of three coordinate Co(II) complexes and the magnitude of negative D values increases with increase in π-accepting ability ligands (Figure 1.8). However, the splitting pattern of the d-orbitals differ from those observed in case of Fe(II) and in ideal trigonal planar geometry. The degenerate orbital pair d_{yz} & d_{xz} has lowest energy while the singly degenerate d_{z²} orbital lies in lower energy as compared to the doubly degenerate d_{xy} & d_{x²-y²} pair. This eventually leads to strong out-of-state SOC and therefore the ZFS parameters of three coordinate Co(II) complexes are found to be large negative in nature.

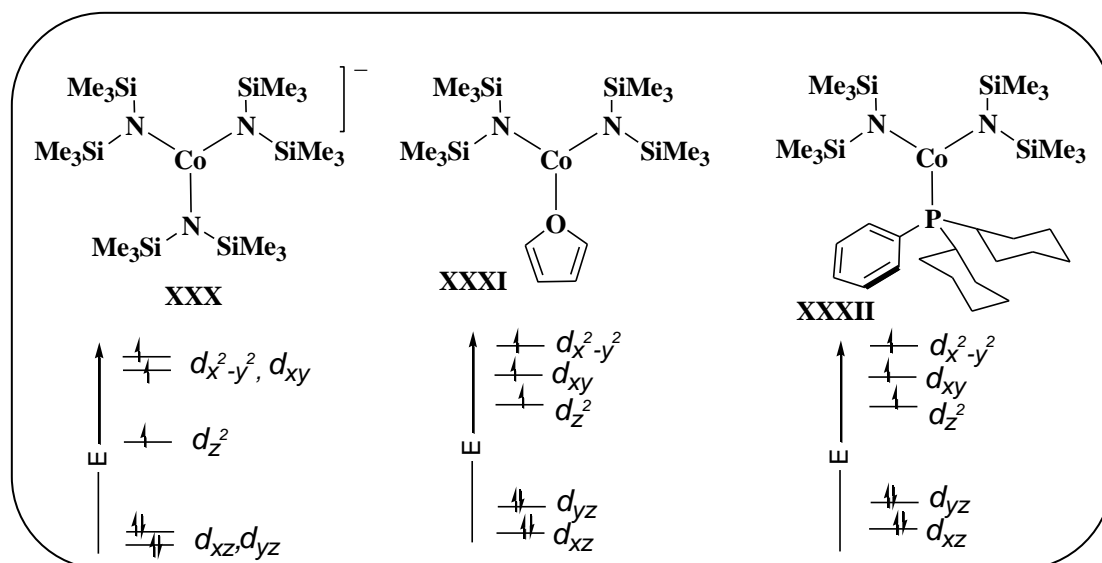


Figure 1.8. Structures of complexes **XXX**, **XXXI** and **XXXII** and their respective d-orbital splitting patterns

1.4. Magnetic anisotropy in four-coordinate complexes

Mononuclear four-coordinate transition metal complexes may acquire tetrahedral (T_d), trigonal pyramidal (C_{3v}) and square planar (D_{4h}) geometries and the splitting pattern of d-orbitals in different geometries is shown in Figure 1.9. Several four-coordinate complexes displaying large values of magnetic anisotropies have been reported in recent years. In general, d^1 , d^3 , d^6 and d^8 ions in trigonal pyramidal geometry show large ZFS due to unquenched orbital angular momentum and possess large negative D value while d^2 and d^7 complexes exhibit a large positive D value. Further, in case of tetrahedral geometry, large negative and large positive ZFS are expected for all d^n ions. Some of the recent investigations dealing with magnetic anisotropy of four-coordinate complexes are discussed below.

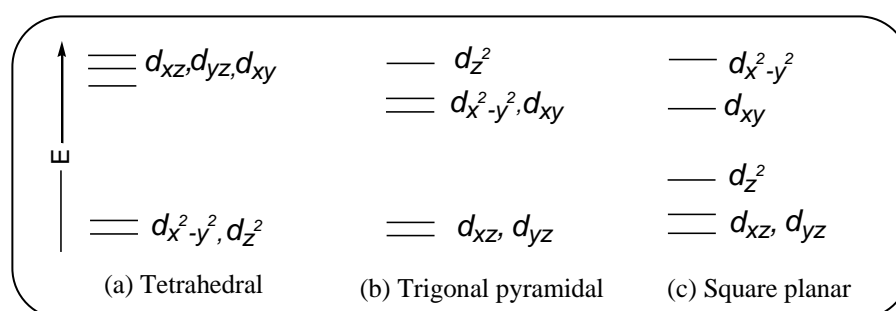


Figure 1.9. Energy level sequence of d-orbitals in four-coordinate complexes in (a) tetrahedral (T_d), (b) trigonal pyramidal (C_{3v}) and (c) square planar (D_{4h}) geometry

Although examples of four-coordinate complexes with trigonal pyramidal geometry are relatively scarce, several such complexes have been recently reported by using sterically rigid ligands which enforces trigonal pyramidal geometry around the central metal ion. The ZFS of several trigonal pyramidal complexes have been investigated and the reported values are listed in Table 1.2. While unprecedentedly large negative ZFS value has been observed for a trigonal pyramidal Ni(II) complex, values as large as -48 cm^{-1} has been reported for Fe(II) complexes.

Table 1.2. Reported D values of mononuclear four-coordinate complexes in trigonal pyramidal geometry

Sl. No.	Complexes	D (cm^{-1})	References
1.	$\text{K}[(\text{tpa}^{\text{Mes}})\text{Fe}].2\text{DME}$ (XXXIX)	-44	48
2.	$\text{K}[(\text{tpa}^{\text{Trip}})\text{Fe}].3\text{DME}$ (XL)	-30	48
3.	$\text{Na}[(\text{tpa}^{\text{Ph}})\text{Fe}].3\text{DME}$ (XLI)	-26	48
4.	$\text{K}[(\text{tpa}^{\text{DFP}})\text{Fe}].2\text{DME}$ (XLII)	-6.2	48
5.	$\text{Na}[(\text{tpa}^{\text{t-Bu}})\text{Fe}].\text{THF}$ (XLIII)	-48	48
6.	$\text{K}[\text{Co}(\text{N}(\text{CH}_2\text{C}(\text{O})\text{NC}(\text{CH}_3)_3)]$ (XLIV)	16	49
7.	$\text{K}[\text{Ni}(\text{N}(\text{CH}_2\text{C}(\text{O})\text{NC}(\text{CH}_3)_3)]$ (XLV)	-200	50

$\text{H}_3\text{tpa}^{\text{DFP}}$: tris(5-2,6-difluorophenyl-pyrrol-2-yl)methyl)amine; $\text{H}_3\text{tpa}^{\text{Mes}}$: tris(5-mesityl-pyrrol-2-yl)methyl)amine; $\text{H}_3\text{tpa}^{\text{Ph}}$: tris(5-phenyl-pyrrol-2-yl)methyl)amine; $\text{H}_3\text{tpa}^{\text{t-Bu}}$: tris(5-tert-butyl-pyrrol-2-yl)methyl)amine; $\text{H}_3\text{tpa}^{\text{Trip}}$: tris(5-2,4,6-triisopropylphenyl-pyrrol-2-yl)methyl)amine

Long and coworkers recently described a family of mononuclear trigonal pyramidal iron(II) complexes supported by tris(pyrrolyl- α -methyl) amine (tpa) ligand of the general formula $[\text{M}(\text{solv})_n][(\text{tpa}^{\text{R}})\text{Fe}]$; $\{\text{M} = \text{K}, \text{R} = \text{mesityl}$ (**XXXIX**), 2,4,6-triisopropylphenyl (**XL**), 2,6-difluorophenyl (**XLII**), $\{\text{M} = \text{Na}, \text{R} = \text{tert-butyl}$ (**XLIII**), phenyl (**XLI**)} [48]. In trigonal pyramidal geometry, ligand field splitting of the d-orbitals results in two doubly degenerate sets $E'(d_{xz}, d_{yz})$ and $E''(xy, x^2-y^2)$ while the singly degenerate term $A_1'(d_z^2)$ is highest in energy. Consequently, the ground state spin for Fe(II) ion in trigonal pyramidal geometry is $S=2$ and three electrons occupy the degenerate E' orbitals as depicted in Figure 1.10. Thus, one can easily envisage that

trigonal pyramidal Fe(II) complexes shall have unquenched orbital angular momentum along the z-direction and therefore, large SOC is expected. Indeed, magnetization measurements revealed that these complexes feature ZFS parameter as large as -48 cm^{-1} as a result of efficient spin orbit mixing. Consequently, large energy barrier for magnetization reversal is expected for these compounds ($U = 192 \text{ cm}^{-1}$) and the effective energy barrier for magnetization reversal obtained from dynamic susceptibility measurements is $U_{\text{eff}} = 65 \text{ cm}^{-1}$. However, due to QTM, the magnetization reversal process is much faster and none of these trigonal pyramidal Fe(II) complex display SMM behaviour in the absence of external dc magnetic field. Apart from this, the ability to enhance the relaxation barrier by manipulating the ligand field has been demonstrated in this study. The D values of mononuclear trigonal pyramidal transition metal complexes reported so far are listed in Table 1.2. The complexes of Fe(II) possess a negative value of D ranging from -6.2 to -48 cm^{-1} , whereas that of Co(II) complex in trigonal pyramidal geometry has a positive D value of 16 cm^{-1} . Moreover, in case of the Ni(II) complex $\text{K}[\text{Ni}(\text{N}(\text{CH}_2\text{C}(\text{O})\text{NC}(\text{CH}_3)_3)]$ (XLV), an unusually large value of D has been observed [50]. In case of trigonal pyramidal d^8 complex, the doubly degenerate E'' set will be occupied by three electrons and therefore considerable in-state SOC is expected. Further, the degeneracy of the E'' set can be partially lifted by Jahn-Teller distortion and this produces an excited state very close to the ground state. Therefore, considerably strong out-of-state SOC is also expected in d^8 complexes trigonal pyramidal geometry which can be attributed to the exceptionally large negative ZFS parameter observed in complex XLV.

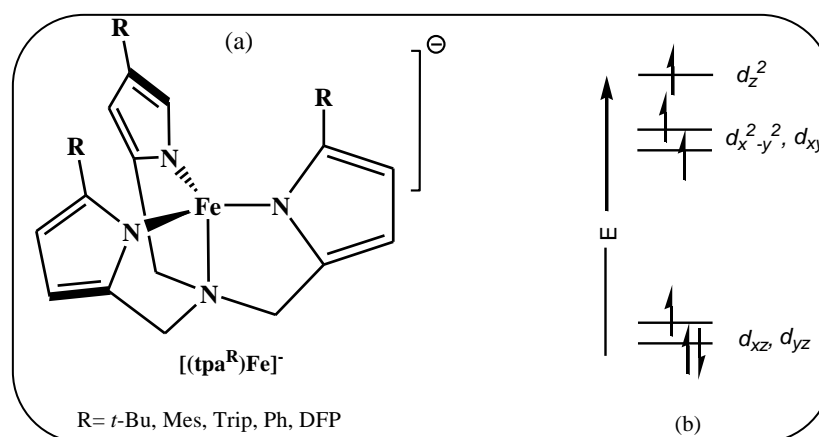


Figure 1.10. (a) Molecular structure of $[(\text{tpa}^{\text{R}})\text{Fe}]^{-}$ (b) Energy level sequence of Fe(II) in these complexes

In view of easy availability of tetrahedral complexes, several studies pertaining to the determination of ZFS in tetrahedral complexes have appeared recently. Indeed, ZFS of several tetrahedral complexes explored so far are found to be reasonably large and therefore most of the recent investigations have primarily focused on understanding the origin of magnetic anisotropy in such complexes. The D values reported for mononuclear four-coordinate tetrahedral complexes have been listed in Table 1.3.

Table 1.3. Reported D values of mononuclear four-coordinate complexes

Sl. No.	Complexes	D (cm ⁻¹)	References
Tetrahedral			
1.	(PPh ₄) ₂ [Co(SPh) ₄] (XLVI)	-74	51
2.	(PPh ₄) ₂ [Co(OPh) ₄] (XLVII)	-11.1	53
3.	(PPh ₄) ₂ [Co(SePh) ₄] (XLVIII)	-83	53
4.	[Co(PPh ₃) ₂ Cl ₂] (XLIX)	-16.2	52
5.	[Co(DPEphos)Cl ₂] (L)	-14.4	52
6.	[Co(Xantphos)Cl ₂] (LI)	-15.4	52
7.	[Co(PPh ₃) ₂ Br ₂] (LII)	-13	54
8.	(PPh ₄) ₂ [Co(C ₃ S ₅) ₂] (LIII)	-161	55
9.	[Co(Bc ^{tBu}) ₂] (LIV)	-3.86	56
10.	[Fe(Bc ^{tBu}) ₂] (LV)	-10.74	56
11.	[(3G)CoCl](CF ₃ SO ₃) (LVI)	12.7	57
12.	[Co(dmph)Br ₂] (LVII)	10.62	58
13.	[PPh ₄] ₂ [Fe(SPh) ₄] (LVIII)	5.84	59
14.	[Fe(N(TMS) ₂) ₂ (depe)] (LIX)	4.1	43
15.	[⁵ CpFe(C ₆ H ₃ ¹ Pr _{2-2,6})] (LX)	-51.36	60
Square planar			
1.	[NBu ₄][Co(C ₆ F ₅) ₄] (LXI)	145	61
2.	[NBu ₄][Co(C ₆ Cl ₅) ₄] (LXII)	93	61

3G: 1,1,1-tris-[2N-(1,1,3,3-tetramethylguanidino)methyl]ethane; dmph: 2,9-dimethyl-1,10-phenanthroline; Bc^{tBu}: bis(3-tert-butylimidazol-2-ylidene)-borate; PCy₃: tricyclohexylphosphine; depe: bidentate 1,2-bis(diethylphosphino)ethane

The D parameters of Co(II) and Fe(II) complexes are found to be significantly influenced by coordination environment around the central metal ions. Some of the investigations on ZFS of mononuclear four-coordinate tetrahedral complexes are discussed below.

The presence of unquenched orbital angular momentum in tetrahedral Co(II) have been realized almost four decades ago, as the effective magnetic moment for Co(II) halides or pseudohalides with distorted tetrahedral geometry were found to be rather large as compared to that predicted by spin only formula. Elaborative single-crystal EPR spectroscopy, computational studies and magnetization measurements have recently revealed that in pseudotetrahedral (D_{2d}) geometry, Co(II) possesses significant magnetic anisotropy and the axial ZFS parameter was found to be -74 cm^{-1} for $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SPh})_4]$ (**XLVI**) (Figure 1.11) [51]. The origin of large magnetic anisotropy in pseudotetrahedral Co(II) complexes can be qualitatively understood by examining the d-orbital energy sequence obtained from angular overlap model (Figure 1.10). The $d_z^2(A_1)$, $d_{x^2-y^2}(B_1)$ and $d_{xy}(B_2)$ orbitals remain non-degenerate while d_{xz} and $d_{yz}(E)$ orbitals are doubly degenerate. The electronic configuration one would expect for Co(II) in D_{2d} geometry, $(d_z^2)^2 (d_{x^2-y^2})^2 (d_{xy})^1 (d_{xz}, d_{yz})^2$ is without any ground state electronic degeneracy and therefore no first order contribution to orbital angular momentum is present. However due to the close proximity of the $d_{x^2-y^2}$ and d_{xy} orbitals, out-of-state SOC is possible and this can be accounted for the large ZFS parameter observed in complex **XLVI**. Due to the non-integer ground state spin $S = 3/2$ which rules out the possibility of QTM and large magnetic anisotropy, it was envisaged that complex **XLVI** should behave as an SMM. Indeed, dynamic susceptibility measurements reported by Zadrozny revealed that complex **XLVI** undergo slow relaxation of magnetization even in the absence of any applied field bias [51]. Following the above study, Zadrozny and coworkers demonstrated the influence of donor atoms on the ZFS of tetrahedral Co(II) complexes by comparing the ZFS value of $(\text{Ph}_4\text{P})_2[\text{Co}(\text{OPh})_4]$ (**XLVII**) with those obtained for $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SPh})_4]$ (**XLVI**) and $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SePh})_4]$ (**XLVIII**) [53]. Results of their investigation revealed that soft donor ligands lead to large magnetic anisotropy as the D value observed for $(\text{Ph}_4\text{P})_2[\text{Co}(\text{OPh})_4]$ (**XLVII**) was significantly small as compared to those observed for $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SPh})_4]$ (**XLVI**) and $(\text{Ph}_4\text{P})_2[\text{Co}(\text{SePh})_4]$ (**XLVIII**).

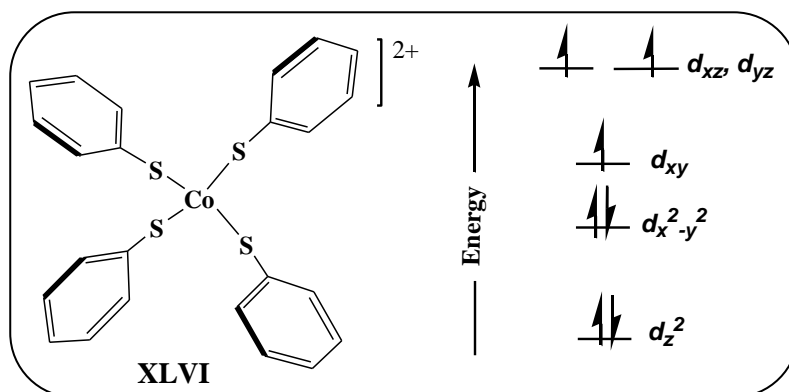


Figure 1.11. Molecular structure and energy sequence of the first reported Co(II) complex **XLVI** showing tetrahedral geometry

Subsequently, two more investigations on the effect of coordination environment on magnetic anisotropy of tetrahedral Co(II) complexes have been reported. Dunbar and Saber reported that using ligands with softer donor atoms leads to an increase in axial ZFS parameter as the D values of [Co(quinolone)₂I₂] (**LXIII**), [Co(PPh₃)₂I₂] (**LXIV**) and [Co(AsPh₃)₂I₂] (**LXV**) are found to be +9.2 cm⁻¹, -36.9 cm⁻¹ and -74.7 cm⁻¹ respectively [62]. Recently, Shanmugan and coworkers also demonstrated that the ZFS parameter of the tetrahedral Co(II) complexes, [Co(L₁)X₂(CH₃CN)] {X = Cl (**LXVI**) and Br (**LXVII**), L₁ : 2,3-diphenyl-1,2,3,4-tetrazolium-5-olate} are +15.61 cm⁻¹ and +11.16 cm⁻¹ respectively. However, the axial ZFS parameters of isostructural complexes, [Co(L₁)X₂(CH₃CN)] {X = Cl (**LXVIII**) and Br (**LXIX**), L₁ = 2,3-diphenyl-1,2,3,4-tetrazolium-5-thiolate} prepared by using a sulphur substituted derivative of L₁ are found to be -11.30 cm⁻¹ and -10.32 cm⁻¹ respectively [63]. Apart from the above, Yang and co-workers investigated ZFS of three mononuclear tetrahedral Co(II) complexes *viz.* [Co(PPh₃)₂Cl₂] (**XLIX**), [Co(DPEphos)Cl₂] (**L**) and [Co(Xantphos)Cl₂]

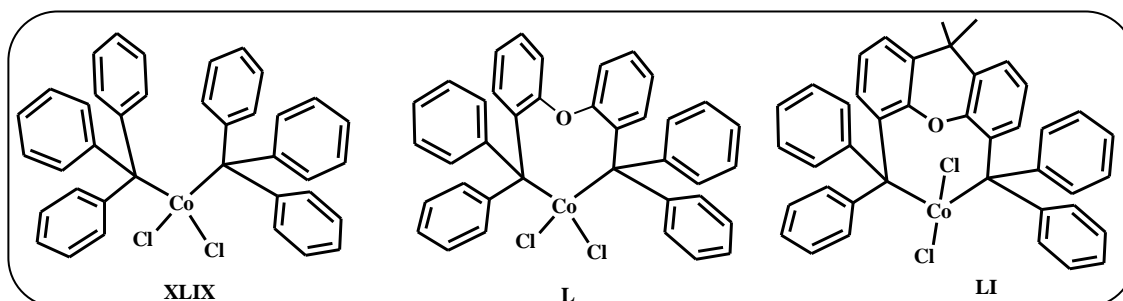


Chart 1.8. Molecular structures of [Co(PPh₃)₂Cl₂] (**XLIX**), [Co(DPEphos)Cl₂] (**L**) and [Co(Xantphos)Cl₂] (**LI**)

(**LI**) {where, PPh₃: triphenylphosphine, DPEphos: 2, 20-bis(diphenylphosphino) diphenyl ether and Xantphos: 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthenes} as shown in Chart 1.8 and their D values are reported as D = -16.2 cm⁻¹, -14.4 cm⁻¹ and -15.4 cm⁻¹ respectively [52].

In comparison to tetrahedral complexes, magnetic anisotropies of square planar complexes are less surveyed and to the best of our knowledge only a couple of studies have been reported so far. García-Monforte and coworkers investigated the axial ZFS in two organometallic Co(III) complexes, [NBu₄][Co(C₆F₅)₄] (**LXI**) and [NBu₄][Co(C₆Cl₅)₄] (**LXII**) and found they possess large positive D values 145 cm⁻¹ and 93 cm⁻¹ respectively [61]. Square planar d⁶ system has singly degenerate ³B₂ ground electronic state and therefore no in-state SOC is possible. However, mixing of the ³B₂ ground state with low lying ³E excited state induces out-of-state SOC. This can be attributed to the presence of large positive ZFS in these compounds. Deng and coworkers recently reported two square planar Cr(II) complexes, [Cr^{II}(N(SiMe₃)₂)₂(L)₂] {L: pyridine (**LXX**) and THF (**LXXI**)}. Field dependence of magnetization studies revealed that the D values of these complexes are -2.01 cm⁻¹ and -2.54 cm⁻¹ respectively [64].

1.5. Magnetic anisotropy in five-coordinate complexes

In recent years, a number of stable five-coordinated complexes have been synthesized and detailed investigations have revealed that many of them possess significantly large magnetic properties. Five-coordinate complexes exist either as square pyramidal (C_{4v}) or more stable trigonal bipyramidal (TBP) (D_{3h}) geometry. The energy level splitting pattern of d-orbitals in five-coordinate complexes are shown in Figure 1.12.

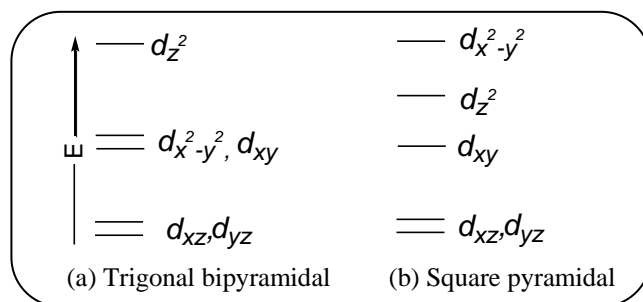


Figure 1.12. Energy level sequence of d-orbitals in five-coordinate complexes in (a) trigonal bipyramidal (D_{3h}) and (b) square pyramidal (C_{4v}) geometries

In TBP geometry, only d^1 and d^6 complexes show large negative D value while d^2 and d^7 ions possess large negative D values. The reported D values of mononuclear five-coordinate complexes are listed in Table 1.4 and studies related to investigation of ZFS in some of the mononuclear five-coordinate complexes are discussed below.

Table 1.4. Reported D values of mononuclear five-coordinate complexes

Sl. No.	Complexes	D (cm^{-1})	References
1.	Mn(bzimpy)Cl ₂ (LXXII)	-2.7	65
2.	[(PNP)FeCl ₂] (LXXIII)	-11	66
3.	[(PNP)Fe(OTf)Cl] (LXXIV)	-6	66
4.	[Co(Me ₆ tren)Cl]ClO ₄ (LXXV)	-8.1	67
5.	[Co(Me ₆ tren)Br]Br (LXXVI)	-4.6	67
6.	[Co(tbta)N ₃]ClO ₄ (LXXVII)	-10.7	68
7.	[Co(DAPDPI)(NCS) ₂] (LXXVIII)	-40.5	69
8.	[Co(DBPDPI)(NCS) ₂] (LXXIX)	-40.6	69
9.	[Co(terpy)Cl ₂] (LXXX)	100	70
10.	[Co(bzimpy)Cl ₂] (LXXXI)	71.7	65
11.	[Co(idppy)Cl ₂] (LXXXII)	71.7	71
12.	[Co(ddppy)Cl ₂] (LXXXIII)	71.7	71
13.	[Co(hdppy)Cl ₂] (LXXXIV)	151	72
14.	[Ni(Me ₆ tren)Cl]ClO ₄ (LXXXV)	-180	78
15.	[Ni(¹ Prtacn)Cl ₂] (LXXXVI)	14	73
16.	[Ni(¹ Prtacn)Br ₂] (LXXXVII)	11	73
17.	[Ni(¹ Prtacn)(NCS) ₂] (LXXXVIII)	13.8	73

bzimpy : 2,6-bis-(benzimidazol-2-yl)-pyridine; ¹Prtacn : 1,4,7-triisoprop-yl-1,4,7-triazacyclononane; Me₆tren : tris(2-(dimethylamino)ethyl)amine; idppy : 4-I-2,6-dipyrazolyl-pyridine; hdppy : 4-1-heptynyl-2,6-dipyrazolyl-pyridine; ddppy : 4-1-dodecynyl-2,6-dipyrazolyl-pyridine; PNP: N[2-P(CHMe₂)2-4-methylphenyl]²⁻; DAPDPI : 2,6-diacetylpyridine-bis-(2,6-diisopropylphen-1-yl)imine; DBPDPI : 2,6-dibenzoylpyridine-bis-(2,6-diisopropylphen-1-yl)imine; tbta : tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine

Five coordinated complexes with square pyramidal geometry are rare and ZFS parameters of only a few such complexes have been reported so far. Presence of large magnetic anisotropy in five-coordinate Co(II) system was initially reported by Boča and co-workers [65]. Recently, Jurca and coworkers reported two air stable Co(II) complexes using the neutral, planar bis(imino)pyridine pincer ligands, [2,6- $\{\text{ArN}=\text{C}(\text{R})\}_2\text{NC}_5\text{H}_3$] (R=Me or Ph) (Chart 1.9) [69].

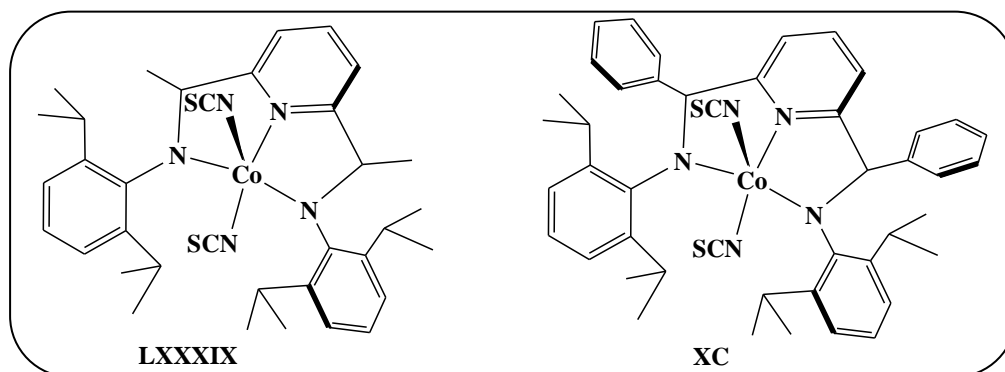


Chart 1.9. Molecular structure of $[\{\text{ArN}=\text{CMe}\}_2(\text{NPh})\text{Co}(\text{NCS})_2$ (**LXXXIX**) and $[\{\text{ArN}=\text{CPh}\}_2(\text{NPh})\text{Co}(\text{NCS})_2$ (**XC**)

The local coordination geometry around the central Co(II) centers in complexes $[\{\text{ArN}=\text{CMe}\}_2(\text{NPh})\text{Co}(\text{NCS})_2$ (**LXXXIX**) and $[\{\text{ArN}=\text{CPh}\}_2(\text{NPh})\text{Co}(\text{NCS})_2$ (**XC**) are distorted square pyramidal and in both the complexes the Co(II) center lies slightly above the basal plane. The R-group of the pincer ligand played a very remarkable role on the geometry of the square pyramidal complex as the central metal ion is more elevated from the basal plane in case of the phenyl substituted complex **XC** as compared to **LXXXIX**. In case of ideal square pyramidal d^7 complex, the degenerate d_{xz} , d_{yz} orbitals will be completely occupied and there is no possibility of in-state SOC. However, distortion of the coordination geometry from ideal square pyramidal by elevation of the central metal ion from the basal plane will lower the energy of d_{xy} orbital while the energy of degenerate d_{xz} , d_{yz} orbitals will increase (Figure 1.13). Thus, the degenerate d_{xz} , d_{yz} orbitals will remain partially filled in distorted square pyramidal geometry and this will induce in-state SOC. Indeed, axial ZFS value of the square pyramidal Co(II) complexes, **LXXXIX** and **XC** deduced from magnetic susceptibility measurements are found to be -28.1 cm^{-1} and -28.2 cm^{-1} respectively.

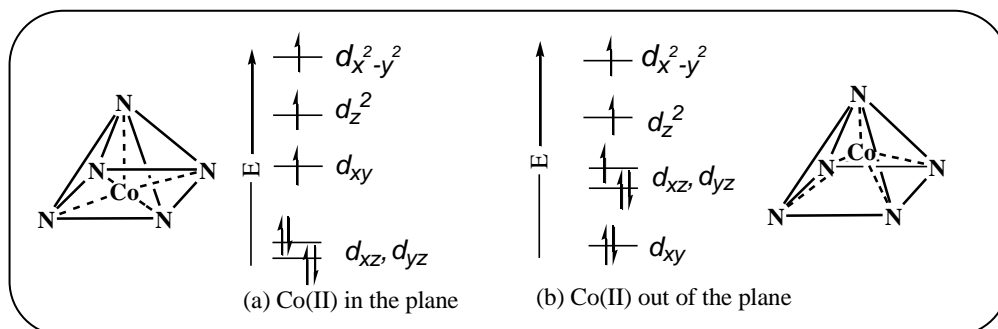


Figure 1.13. Splitting pattern of d-orbitals in square pyramidal geometry with of Co(II) ion (a) in the plane and (b) out of the basal plane

However, magnetization measurement of another distorted square pyramidal Co(II) complex, $[\text{Co}(\text{hdppy})\text{Cl}_2]$ (**LXXXIV**) (hdppy: 4-hept-1-ynyl-2,6-dipyrazol-1-ylpyridine) establish its axial ZFS parameter to be 151 cm^{-1} [72]. Recently, Mondal and coworkers synthesized two isostructural square pyramidal Co(II) complexes, $[\text{Co}(\text{PP}_3)\text{Cl}]\cdot\text{ClO}_4$ (**XCI**) and $[\text{Co}(\text{PP}_3)\text{Br}]\cdot\text{ClO}_4$ (**XCII**) by using a tetradentate ligand tris[2-(diphenylphosphino)ethyl]phosphine (PP_3) [74]. Magnetization studies and theoretical calculations have revealed that the axial ZFS values of complexes **XCI** and **XCII** are 46.4 cm^{-1} and 40.7 cm^{-1} respectively.

Recently, Murugesu and coworkers investigated the influence of coordination geometry around the central metal ion on magnetic anisotropy of mononuclear five-coordinated Co(II) complexes (Figure 1.14) [70]. The coordination geometry around the Co(II) centers in $[\text{Co}(\text{terpy})\text{Cl}_2]$ (**LXXX**) and $[\text{Co}(\text{terpy})(\text{NCS})_2]$ (**XCIII**) are distorted square pyramidal and TBP respectively. Lower energy barrier for magnetization reversal observed in $[\text{Co}(\text{terpy})(\text{NCS})_2]$ (**XCIII**) as compared to that obtained for $[\text{Co}(\text{terpy})\text{Cl}_2]$ (**LXXX**) was attributed to the deviation in symmetry around the Co(II) center.

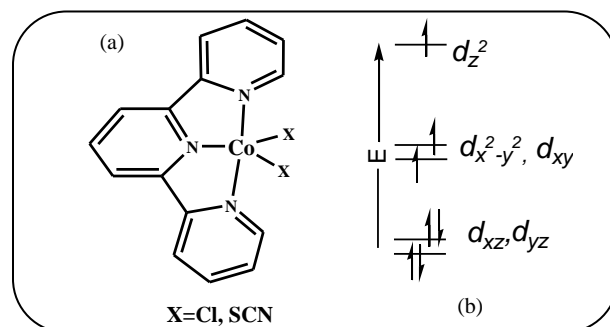


Figure 1.14. Molecular structure and energy sequence of the Co(II) complexes **LXXX** and **XCIII**

Interestingly, two TBP Co(II) complexes, $[\text{Co}(\text{Me}_6\text{tren})\text{Cl}]\text{ClO}_4$ (**LXXV**) and $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (**LXXVI**) reported by Mallah and coworkers showed large uniaxial magnetic anisotropy and associated slow relaxation of magnetization. Low temperature magnetization studies, high frequency EPR as well as theoretical calculations established that $[\text{Co}(\text{Me}_6\text{tren})\text{Cl}]\text{ClO}_4$ (**LXVIII**) and $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (**LXIX**) have D parameters -8.1 cm^{-1} and -4.6 cm^{-1} respectively [67]. Theoretical calculations established that the origin of uniaxial magnetic anisotropy is out-of-state SOC. Further, magnetostructural correlations of these two TBP Co(II) complexes also revealed that weak σ -donating equatorial ligand and strong π -donating axial ligands induces larger axial ZFS. Subsequently, Mallah and coworkers systematically investigated the influence of weak σ -donating equatorial ligand as well as strong π -donating axial ligands on the axial ZFS parameter of TBP Co(II) complexes. Thus, the TBP Co(II) complex, $[\text{Co}(\text{NS}_3^{\text{iPr}})\text{Cl}](\text{BPh}_4)$ (where NS_3^{iPr} = tris(2-(isopropylthio)ethyl)amine) with longer equatorial metal-ligand bond distance shows a considerably larger D value of -23 cm^{-1} as compared to the N-substituted congeners, $[\text{Co}(\text{Me}_6\text{tren})\text{Cl}]\text{ClO}_4$ (**LXVIII**) and $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (**LXIX**) [75]. The influence of axial ligand on ZFS parameter of TBP Co(II) has been recently probed and it was found that the D value of $[\text{Co}(\text{NS}_3^{\text{tBu}})(\text{NCS})]^+$ (**XCIV**) ($D = -11 \text{ cm}^{-1}$) was half the magnitude as compared to $[\text{Co}(\text{NS}_3^{\text{tBu}})\text{Cl}]^+$ (**XCIV**) and $[\text{Co}(\text{NS}_3^{\text{tBu}})\text{Br}]^+$ (**XCVI**) ($D \approx -20 \text{ cm}^{-1}$) [76]. The primary negative contribution to D parameter in TBP Co(II) comes from the SOC of the ground $^4\text{A}_2$ state with a quadruplet excited state, $^4\text{A}_1$ while SOC of the ground state with the excited state ^4E has a small positive contribution towards D. The excited state $^4\text{A}_1$ is obtained by excitation of an electron from (d_{xz}, d_{yz}) to $(d_{x^2-y^2}, d_{xy})$ and therefore weak σ -donating equatorial ligands or strong σ/π -donating axial decreases the energy difference between the ground $^4\text{A}_2$ state and excited $^4\text{A}_1$ state. This eventually leads to stronger SOC between these states and thereby induces larger axial ZFS.

Large magnetic anisotropy in square pyramidal Ni(II) complexes have been realized almost a decade ago, as high field EPR and frequency domain magnetic resonance spectroscopy revealed that the magnitude of axial ZFS parameters in the complexes, $[\text{Ni}(\text{Prtacn})\text{X}_2]$ {X=Cl (**LXXXVI**), Br(**LXXXVII**), NCS(**LXXXVI**); Prtacn : 1,4,7-triisopropyl-1,4,7-triazacyclononane} lies around 15 cm^{-1} [73]. More recently, Mallah and coworkers reported axial ZFS parameter of another square pyramidal Ni(II)

complex, $[\text{Ni}(\text{Me}_4\text{cyclam})\text{N}_3]\text{ClO}_4$ (**XCVII**) (Me_4cyclam : tetramethylcyclam) by using magnetization, EPR and theoretical studies and found that the D parameter of this complex **XCVII** is close to 22 cm^{-1} [77]. In contrast to square pyramidal Ni(II) complexes, the axial ZFS value of TBP Ni(II) complexes are found to be several folds higher and the theoretically estimated D value in ideal D_{3h} geometry for Ni(II) lies close to -600 cm^{-1} . High field EPR studies performed on single crystals of $[\text{Ni}(\text{Me}_6\text{tren})\text{Cl}]\text{ClO}_4$ (**LXXXV**) and $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ (**XCVIII**) established that their axial ZFS parameter lie between -120 cm^{-1} and -180 cm^{-1} respectively [78]. The doubly degenerate triplet ground state, 3E undergoes Jahn-Teller distortion and therefore observed D values are considerably smaller than that calculated for ideal D_{3h} structure. Nevertheless, Murrie and coworkers recently reported high field EPR studies on a TBP Ni(II) complex, $[\text{Ni}(\text{MDABCO})_2\text{Cl}_3]\text{ClO}_4$ (**XCIX**) {MDABCO: 1-Methyl-4-aza-1-azoniabicyclo[2.2.2]octanium iodide} with a negative D value of -535 cm^{-1} and this remains the highest axial ZFS parameter observed for any transition metal complex [79].

1.6. Magnetic anisotropy in six-coordinate complexes

Most 3d transition metal ions prefer six coordinate environment to stabilize their first coordination sphere. Six-coordinate complexes prefer octahedral (O_h) and tetragonal geometries and the energy level sequence of d-orbitals has been depicted in Figure 1.15. Although magnetic anisotropy of six-coordinate complexes are under intense investigation, very few of them possess significant magnetic anisotropy. As reported earlier, due to crystal field splitting and Jahn-Teller effect, the orbital angular momentum of ground electronic state in O_h and D_{4h} (distorted octahedral) complexes

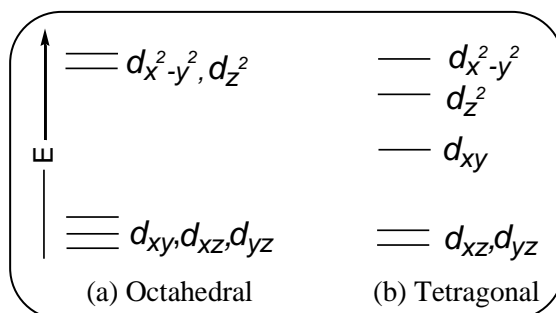


Figure 1.15. Energy level sequence of d-orbitals in six-coordinate complexes in (a) octahedral (O_h) and (b) Tetragonal (I) geometries

are quenched to large extent and out-of-state SOC can only induce magnetic anisotropy in such complexes. Nevertheless, d^1 , d^2 , d^6 and d^7 ions are expected to possess large negative as well as positive magnetic anisotropy in octahedral geometry. Table 1.5 portrays D values shown by the mononuclear hexacoordinated 3d metal complexes. Some of the reported six-coordinate complexes are discussed below.

Table 1.5. Reported D values of some mononuclear six-coordinate 3d metal complexes

Sl. No.	Complexes	D (cm^{-1})	References
1.	$[(\text{PY5Me}_2)_4\text{V}_4\text{Cr}(\text{CN})_6][(\text{CF}_3\text{SO}_3)_5]$ (C)	-0.29	80
2.	$[\text{MnL}]$ (L: 2,4-di-tert-butylphenol) (CI)	1.65	81
3.	$[\text{Mn}(5\text{-TMAM}(\text{R})\text{salmen})\text{Co}(\text{CN})_6]$ (CII)	-3.3	82
4.	$[\text{Mn}((\text{OPPh}_2)_2\text{N})_3]$ (CIII)	-3.4	83
5.	$\text{PPh}_4[\text{Mn}(\text{opbaCl}_2)(\text{py})_2]$ (CIV)	-3.42	84
6.	$\text{Na}_5[\text{Mn}(\text{L-tartarate})_2]$ (CV)	-3.23	85
7.	$[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (CVI)	-14.8	86
8.	cis- $[\text{Co}(\text{dmph})_2(\text{NCS})_2]$ (CVII)	98	87
9.	$[\text{Co}(\text{abpt})_2(\text{tcm})_2]$ (CVIII)	48	88
10.	$[\text{Co}(\text{oda})(\text{aterpy})]$ (CIX)	-7.44	89
11.	$[\text{Fe}(\text{iPr}_5\text{C}_5)(2,6\text{-}^1\text{Pr}_2\text{C}_6\text{H}_3)]$ (CX)	-72.9	90
12.	$[\text{Ni}(\text{HIM2-py})_2\text{NO}_3]\text{NO}_3$ (CXI)	10.15	91

PY5Me₂: 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine; 5-TMAM-(R)-salmen²⁻: (R)-N,N-(1-methylethylene)bis(5-trimethyl ammonio methyl salicyl idene iminate); H₄opbaCl₂: N,N-3,4-dichloro-o-phenylenebis(oxamic acid); ptz : 1-propyltetrazole; dmph : 2,9-dimethyl-1,10-phenantroline; abpt: 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole; tcm : tricyanomethanide anion; oda²⁻ : oxodiacetate; aterpy : 4-azido2,2:6,2-terpyridine; HIM2-py : 4,4,5,5-tetramethyl-2-(2-pyridyl)-2-imidazoline-1,3-diol; py: pyridine; Ph₄P⁺: tetraphenylphosphonium cation

Several mononuclear Mn(III) complexes (d^4) has been reported to exhibit significant magnetic anisotropy. In a six-coordinated high-spin d^4 complex in octahedral geometry, the ground electronic term $^5\text{E}_g$ is orbitally degenerate. Jahn-Teller effect breaks the orbital degeneracy and splits the $^5\text{E}_g$ term into lower energy states $^5\text{A}_{1g}$ and $^5\text{B}_{1g}$. The

intermingling of these two states results in second order SOC and can induce reasonably large axial magnetic anisotropy. However, the axial ligands attached to the metal centers influence the sign of the magnetic anisotropy. Cano and Pardo have reported the first example of a mononuclear manganese(III) complex, $\text{Ph}_4\text{P}[\text{Mn}(\text{opbaCl}_2)(\text{py})_2]$ (**CIIV**) exhibiting a field-induced slow magnetic relaxation behaviour with a D value of -3.42 cm^{-1} [84].

Another octahedral Mn(IV) complex, $\text{Na}_5[\text{Mn}(\text{L-tartarate})_2] \cdot 12\text{H}_2\text{O}$ (**CV**) was reported by Murrie and coworkers in 2015 with almost similar D value of -3.23 cm^{-1} as a result of Jahn-Teller distortion and subsequent out-of-state SOC [85]. Zlatar and coworkers carried out a systematic study on magnetic anisotropy of a series of mononuclear octahedral Mn(IV) complexes with different coordination environment by using both experimental and theoretical studies. Although, the D values of these complexes were found to lie between -0.99 cm^{-1} to 2.28 cm^{-1} , no concrete magnetostructural rationalization regarding the influence of coordination environment on magnetic anisotropy could be established [92].

In 2013, Long and coworkers have reported the octahedral Fe(II) complex, $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (**CVI**) (Chart 1.10) with a reasonably large D value of -14.8 cm^{-1} [86]. Another six-coordinate Fe(II) complex, $[\text{Fe}(\text{iPr}_5\text{C}_5)(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]$ (**CX**) has been reported by Ruiz and coworkers. Magnetic characterization revealed the value of D to be large negative value of -72.9 cm^{-1} [90].

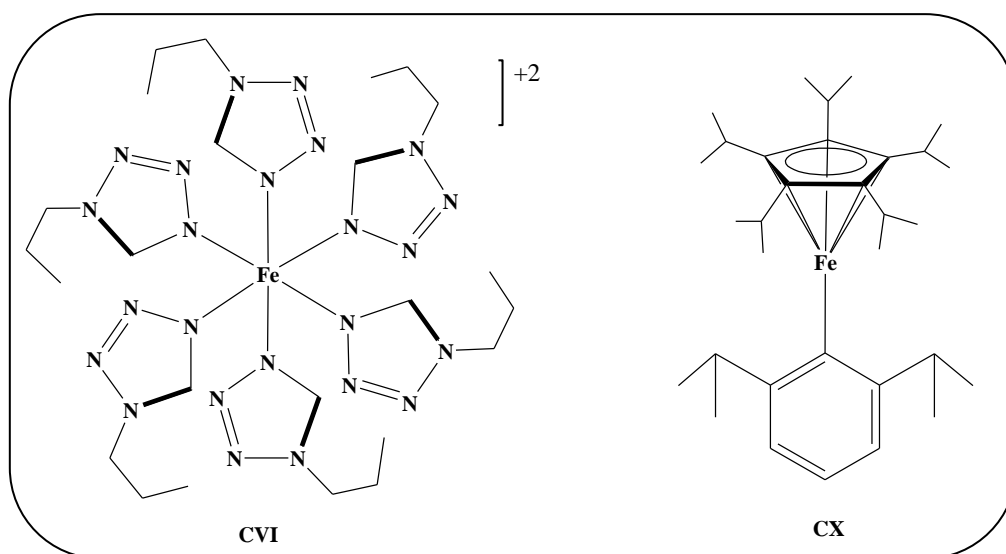


Chart 1.10. Structures of complexes **CVI** and **CX**

1.7. Magnetic anisotropy in seven-coordinate complexes

Seven coordinate complexes are known to exhibit several geometries such as heptagonal (D_{7h}), hexagonal pyramidal (C_{6v}), pentagonal bipyramidal (PBP) (D_{5h}), capped octahedron (C_{3v}), capped trigonal prism (C_{2v}), Johnson pentagonal bipyramidal J13 (D_{5h}), Johnson elongated triangular pyramidal J7 (C_{3v}), of which complexes with PBP geometry is more frequently observed. Since the d-orbital splitting pattern in ideal PBP geometry is identical to that in TBP geometry as shown in Figure 1.14, magnetic anisotropy in PBP geometry also anticipated to be somewhat similar to that observed in TBP geometry.

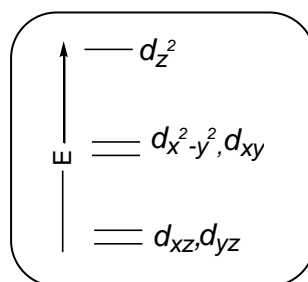


Figure 1.16. Energy level sequence of d-orbitals in seven-coordinate PBP complexes

Magnetic anisotropy in high spin Mn(II) ion with d^5 electronic configuration are expected to be negligible in PBP geometry. In spite of that several studies on ZFS of PBP Mn(II) complexes have been reported so far in order to rationalize D values against the coordination environment around the Mn(II) centers. The primary objective of such ZFS based magneto-structural correlation is to decipher structural information of metalloenzymes where Mn(II) ions are present in active sites e.g. superoxide dismutase, etc. The magnetic anisotropy of a high spin Mn(II) complex, $[\text{MnL}(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (**CXII**) (L: 2,13-dimethyl-3,6,9,12,18-pentaaza bicyclo [12.3.1] octadeca-1(18),2,12,14,16-pentaene) in PBP geometry was investigated by Sosa-Torres and co-workers in 1998 [93]. The D value of this complex has been found to be 0.07 cm^{-1} by using spectral analysis and theoretical calculations. In 2010, Collomb and co-workers investigated ZFS parameters of a series of mononuclear Mn(II) complexes by EPR spectroscopy and quantum chemical calculations [94]. The results illustrates that value of D for the two seven-coordinate complexes $[\text{Mn}(\text{terpy})-(\text{NO}_3)_2(\text{H}_2\text{O})]$ (**CXIII**) (terpy: 2,2'':6,2''-terpyridine) and $[\text{Mn}(\text{bpea})(\text{NO}_3)_2]$ (**CXIV**) (bpea: *N,N*-bis(2-pyridylmethyl)ethylamine) with N_3O_4 coordination environment are -0.068 cm^{-1} and

0.086 cm^{-1} respectively [95]. Moreover, Kersting and coworkers have reported the synthesis and magnetic properties of another PBP Mn(II) complex, $[\text{Mn}(\text{HL}_2)(\text{H}_2\text{O})(\text{EtOH})]\text{BPh}_4$ (**CXV**) (L: 2,6-diacetyl-4-carboxymethyl-pyridine bis(benzoylhydrazone)). The D value for this distorted PBP complex has been found to be 0.61 cm^{-1} [96].

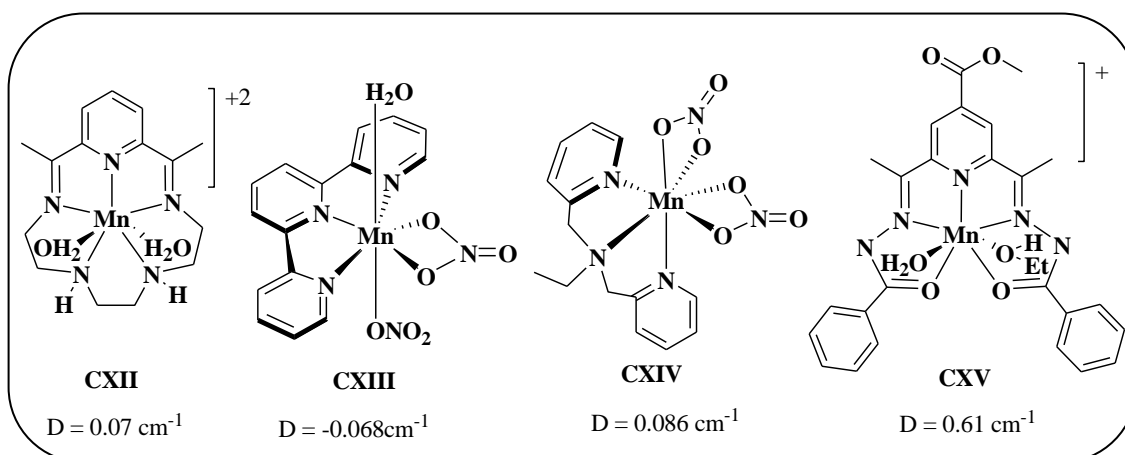


Chart 1.11. Structures of reported PBP Mn(II) complexes

Presence of spin orbit coupling in a high-spin Fe(II) ion (d^6) in PBP geometry leads to large uniaxial magnetic anisotropy. SOC between the partially filled d_{xz} and d_{yz} orbitals is responsible for the presence of magnetic anisotropy in PBP Fe(II) complexes. The structures of the seven-coordinate PBP Fe(II) complexes for which ZFS have been investigated are depicted in Chart 1.12. Sutter and coworkers investigated magnetic anisotropy of Fe(II) in hepta-coordinated PBP geometry and observed that the complex $[\text{Fe}(\text{L}_1)(\text{H}_2\text{O})_2]\text{Cl}_2$ (**CXVI**) $\{\text{L}_1: 2, 13\text{-dimethyl-3, 6, 9, 12, 18\text{-pentaazabicyclo [12.3.1] octadeca-1(18),2,12,14,16\text{-pentaene}}\}$ possesses reasonably large negative ZFS parameter, $D = -17.2 \text{ cm}^{-1}$ [97]. Yet again, in 2015, Sutter and coworkers used an acyclic bis-hydrazone ligand to prepare two heptacoordinated Fe(II) complexes with PBP geometry, $[\text{Fe}(\text{H}_2\text{L})(\text{H}_2\text{O})(\text{MeOH})].2\text{MeOH}.2\text{BF}_4$, (**CXVII**) and $[\text{Fe}(\text{H}_2\text{L})\text{Cl}_2].0.5\text{MeOH}$ (**CXVIII**) $\{\text{L}: 2, 6\text{-diacetyl pyridine bis-(benzoyl hydrazone)}\}$ [98]. Low temperature magnetization measurements reveal that complex **CXVIII** shows a negative D value of -13.3 cm^{-1} while for complex **CXVII**, good fitting of magnetization data with acceptable set of parameters was not obtained. Recently, Sutter and coworkers reported two more PBP Fe(II) complexes

$[\text{Fe}(\text{H}_2\text{L}^*)(\text{MeOH})\text{Cl}]\text{Cl}\cdot\text{MeOH}$ (**CXIX**) $\{\text{L}^*: 2, 6\text{-diacetyl pyridine bis}(\text{biphenyl hydrazone})\}$, $[\text{Fe}(\text{H}_2\text{L}')\text{Cl}_2]$ (**CXX**) $\{\text{L}': 2, 6\text{-diacetyl pyridine bis}(\text{semicarbazone})\}$ (Chart 1.12) [99]. Magnetization measurements revealed that the values of ZFS parameter D are -6.3 and -13.0 cm^{-1} for complexes **CXIX** and **CXX** respectively. Moreover, they have also reported the value of D for the complex **CXVII** as -4.0 cm^{-1} .

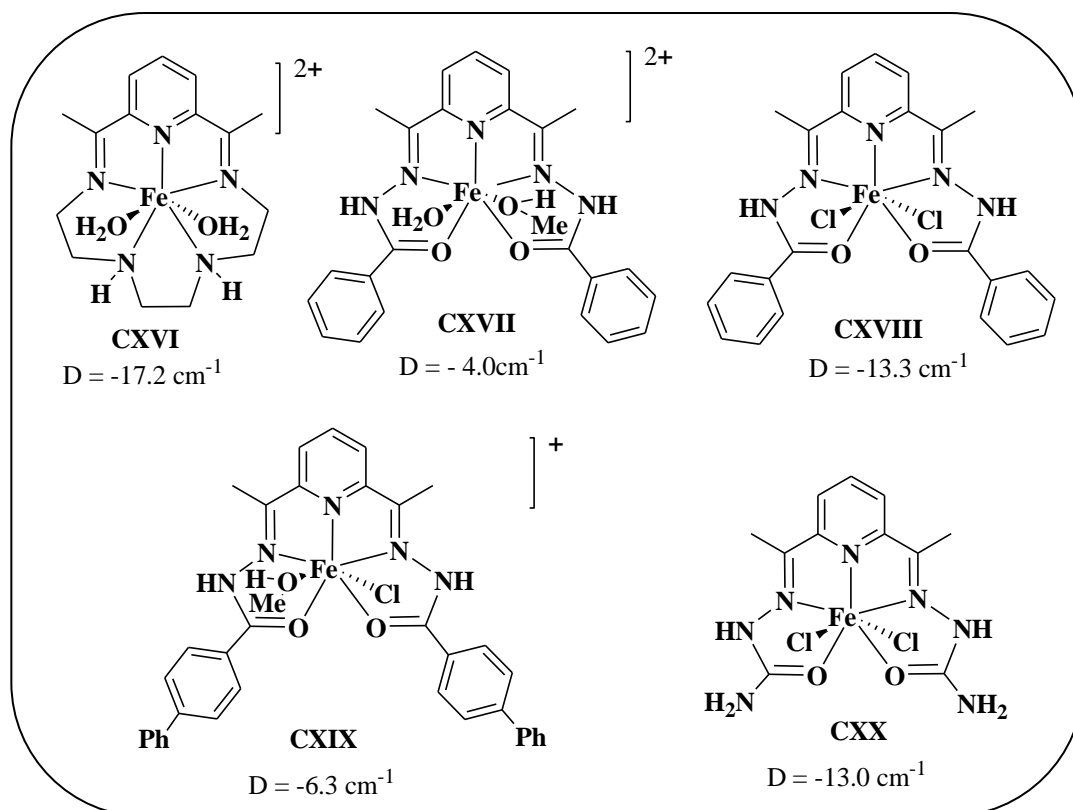


Chart 1.12. Structures of the reported seven coordinate Fe(II) complexes

Large magnetic anisotropy has been observed in several seven-coordinate PBP Co(II) complexes and in all cases the D values are found to be large positive in nature. ZFS values of all PBP Co(II) complexes reported till date have been depicted in Chart 1.13. The highest D value of Co(II) complexes in PBP geometry has been reported by Turta and co-workers in 2012 for $[\text{Co}(\text{bpy})_{1.5}(\text{NO}_3)_2]$ (**CXXI**) (bpy: 4,4'-bipyridine) [100]. Magnetization measurements of this PBP complex, **CXXI** shows that it has large ZFS value of $D = 68.7 \text{ cm}^{-1}$. In 2015, a large value of $D = 45 \text{ cm}^{-1}$ has been reported by Trávníček and co-workers for a Co(II) complex, $[\text{CoL}^\# \text{Cl}_2]$ (**CXXII**) prepared by using a 15-membered pyridine-based macrocycle ($\text{L}^\#$: 3,12,18-triaza-6,9-

dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene) [101]. Subsequently, Chen and co-workers reported two mononuclear PBP Co(II) complexes, $[\text{Co}(\text{L}^\dagger)_3(\text{NO}_3)_2]$ $\{\text{L}^\dagger: 4\text{-tert-butylpyridine, (CXXIII); L}^\dagger: \text{isoquinoline, (CXXIV)}\}$. Detailed analysis of their magnetic susceptibility measurements confirms the presence of slow relaxation of magnetization and the magnitude of D values for the complexes **CXXIII** and **CXXIV** are found to be 35.8 and 35.7 cm^{-1} respectively [102]. Trávníček and coworkers in 2016 have reported another mononuclear Co(II) complex, $[\text{Co}(\text{L}^\ddagger)](\text{ClO}_4)_2$ (**CXXV**) with distorted PBP geometry $\{\text{L}^\ddagger: 3,12\text{-bis}(2\text{-methylpyridine})\text{-}3,12,18\text{-triazas}-6,9\text{-dioxabicyclo [12.3.1]octadeca-1,14,16-triene}\}$ [103]. Fitting of the magnetization measurements data gives a large value of $D = 34 \text{ cm}^{-1}$ for complex **CXXV**. Moreover, Mallah and coworkers reported D values of three mononuclear PBP Co(II) complexes, $[\text{Co}(\text{H}_2\text{L})\text{X}(\text{H}_2\text{O})]\text{X}$ $\{\text{X} = \text{NO}_3$ (**CXXVI**), Br (**CXXVIII**), I (**CXXIX**) $\}$ prepared by using an acyclic bis-hydrazone ligand, H_2L ($\text{H}_2\text{L} = 2,6\text{-diacetyl pyridine bis}(\text{benzoyl hydrazine})$) [104]. The complexes are found to be highly magnetically anisotropic and the D values are found to be independent of the nature of the axial ligands. Recently, Sutter and coworkers have reported another PBP Co(II) complex, $[\text{Co}(\text{H}_2\text{L}^*)(\text{MeOH})(\text{NO}_3)]\text{NO}_3 \cdot \text{MeOH}$ (**CXXVII**) $\{\text{L}^*: 2,6\text{-diacetyl pyridine bis}(\text{biphenyl hydrazone})\}$ and found $D = 33.4 \text{ cm}^{-1}$ by fitting the magnetization data of the complex **CXXVII** [99]. Moreover, Kersting and coworkers in 2011 have reported the synthesis and magnetic properties of a mononuclear PBP Co(II) complex, $[\text{Co}(\text{H}_2\text{L})(\text{H}_2\text{O})(\text{EtOH})]\text{BPh}_4$ (**CXXX**) $\{\text{L}: 2,6\text{-diacetyl-}4\text{-carboxymethyl-pyridine bis}(\text{benzoylhydrazone})\}$ [96]. Fitting of the magnetization data showed that $D = 27.65 \text{ cm}^{-1}$ for the complex **CXXX**. More recently, Wang and coworkers have observed field-induced slow magnetic relaxation for air-stable mononuclear PBP cobalt(II) compounds, $[\text{Co}(\text{H}_2\text{L})(\text{im})_2] \cdot \text{H}_2\text{O}$ (**CXXXI**) and $[\text{CoL}_{\text{N}_5}(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (**CXXXII**) $\{\text{L}: 2,6\text{-diacetyl pyridine bis}(\text{benzoyl hydrazone}); \text{L}_{\text{N}_5}: 2,13\text{-dimethyl-}3,6,9,12\text{-tetraaza-}1(2,6)\text{-pyridinacyclo}[\text{tridecaphane-}2,12\text{-diene, im: imidazole}\}$ [105]. These complexes are reported to be the first examples seven-coordinated mononuclear 3d metal compounds showing SMM behaviour with $D = 24.8$ and 24.6 cm^{-1} for complexes **CXXXI** and **CXXXII** respectively [101]. Thus, the above examples clearly establish the presence of large magnetic anisotropy in PBP Co(II) complexes.

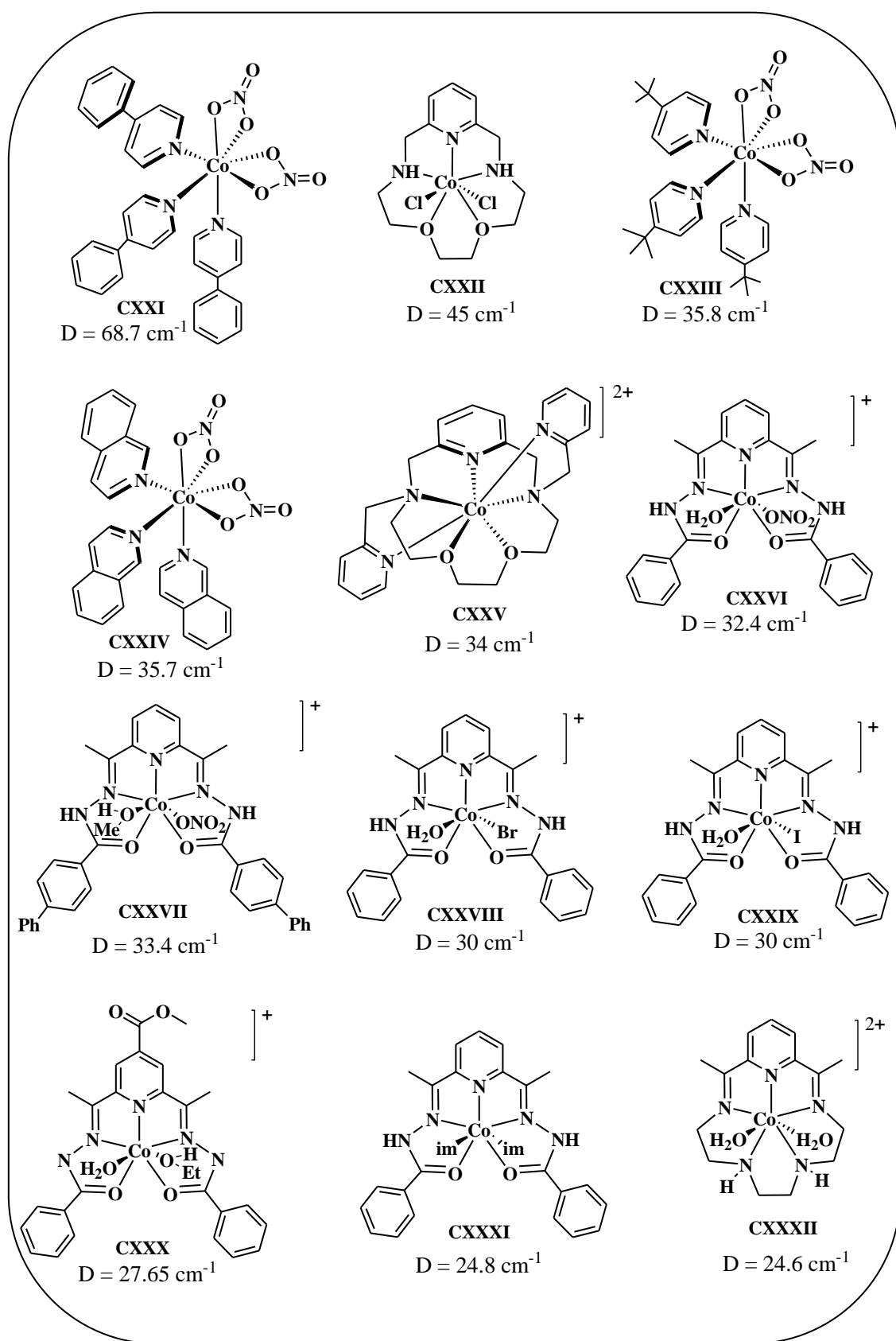


Chart 1.13. Structures of the reported seven coordinate Co(II) complexes

In 2013, Sutter and co-workers assembled two hepta-coordinated PBP Ni(II) compounds, $[\text{Ni}(\text{H}_2\text{L})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ and $[\text{Ni}(\text{H}_2\text{L}^*)(\text{MeOH})(\text{NO}_3)]\text{NO}_3$ (**CXXXIII** and **CXXXIV**) [106]. The structures of these Ni(II) complexes have been shown in Chart 1.14. Modelling of the field dependence of magnetization revealed the value of D to be -13.9 and -12.5 cm^{-1} for complexes **CXXXIII** and **CXXXIV** respectively. Recently, Sutter and coworkers again reported the magnetization measurement of another PBP Ni(II) complex, $[\text{Ni}(\text{H}_2\text{L}')(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**CXXXV**) and the value of D is found to be -12.5 cm^{-1} [99].

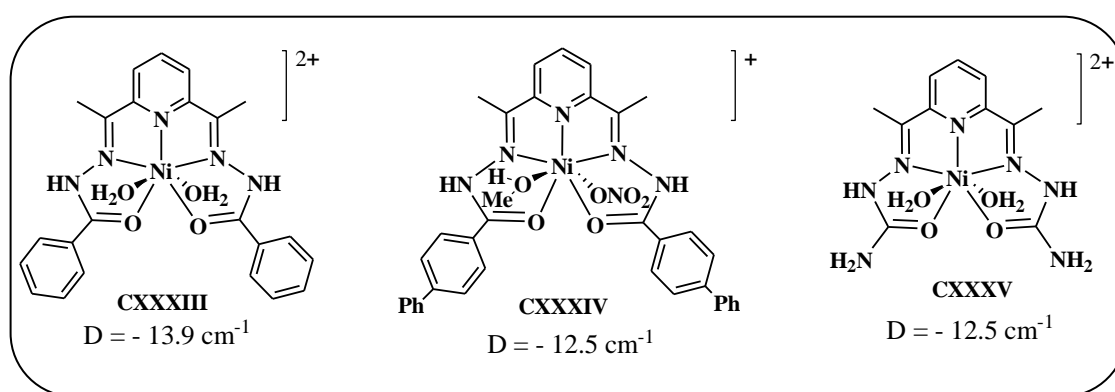


Chart 1.14. Structures of the Ni(II) complexes **CXXXIII**, **CXXXIV** and **CXXXV**

Apart from the above, only three other Ni(II) complexes in PBP geometry have been reported to the best of our knowledge. Trávníček and coworkers in 2015 reported another seven-coordinate Ni(II) complex, $[\text{Ni}(\text{L})\text{Cl}_2]$ (**CXXXVII**) (L: 3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-triene) and the ZFS parameter of this complex has been determined to be $D = -6.08$ cm^{-1} from the variable temperature magnetization measurements. Recently, the same group have synthesized and characterized another Ni(II) complex, $[\text{Ni}(\text{L})](\text{ClO}_4)_2$ (**CXXXVI**) in PBP geometry using the ligand 3,12-bis(2-methylpyridine)-3,12,18-triaza-6,9-dioxabicyclo[12.3.1]octadeca-1,14,16-triene [107]. Best fit of the magnetization susceptibility data gives $D = -12.8$ cm^{-1} for complex **CXXXVI**. In 2005, Rodríguez-Blas and co-workers have successfully synthesized a distorted PBP Ni(II) complex using N,N'-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (**CXXXVIII**) (Chart 1.15) [108]. Detailed experimental and theoretical investigations revealed that the value of D is 15 cm^{-1} for complex **CXXXVIII**.

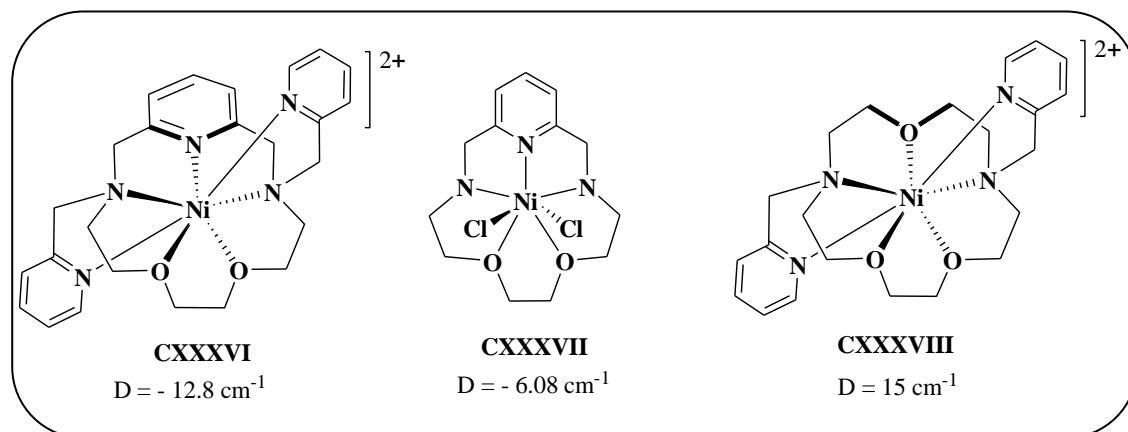


Chart 1.15. Structures of the cationic units of Ni(II) complexes **CXXXVI**, **CXXXVII** and **CXXXVIII**

1.8. Objectives of Present Work

Detailed literature survey on ZFS parameters reported for two- to seven-coordinate single-ion transition metal complexes revealed that very few species with large negative D parameter is available so far. However, majority of the above studies did not investigate the role of coordination environment on ZFS parameter. In case of high coordinate species described above, magnetic anisotropy primarily originated from the out-of-state SOC. Since the energy of the excited states involved in SOC can be modulated by proper choice of coordination environment around the metal center, in principle it should also allow us to mediate the magnitude as well as sign of D parameters. In view of the above, we endeavoured to perform a systematic study on the variation of ZFS parameter by subtle modification of the coordination environment. PBP complexes formed by the bis-hydrazone ligand, 2,6-diacetylpyridine bis(benzoyl hydrazone) was chosen for this purpose as this allows us to change both the axial and equatorial coordination environments around the central metal ion without deviating from the PBP geometry. Further, ZFS values of several PBP complexes formed by this ligand have been already reported and this allows us to compare our results with the reported studies. One of the most appealing features of PBP complexes is their ability to act as building blocks for heterometallic polynuclear assemblies and this presents an unique opportunity to develop magnetically enticing systems. There is a possibility to replace the axial coordination sites of PBP complexes by using metalloligands and this will eventually result in heterometallic aggregates. In view of the fascinating

assortment of intriguing magnetic features displayed by cyanometallate based assemblies, we endeavored to employ cyanometallate based linkers to interconnect magnetically anisotropic PBP complexes. It is anticipated that cyano groups of the linkers will replace the axial sites of PBP complexes and thereby result heterometallic aggregates. Thus, the primary objectives of the present thesis can be outlined as:

- [1] Preparation of pentagonal bipyramidal complexes of paramagnetic transition metal ions. Characterization of the new PBP complexes by using analytical, spectroscopic and structural tools.
- [2] Investigating the magnetic anisotropy in pentagonal bipyramidal complexes by using magnetization measurements and DFT based theoretical calculations.
- [3] Assembling heterobimetallic species using the PBP complexes as building blocks and cyanometallate based metalloligands as linkers. Characterization of the heterometallic species by using analytical, spectroscopic and structural investigations.
- [4] Investigation of static and dynamic magnetic properties of the cyano bridged heterometallic species at low temperatures and carry out magnetostructural correlations.

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