Chapter 1

Introduction

1.1 Motivation

Research Philosophy

Major research interest in the Powell group is the synthesis and characterisation of Molecular Nano-Magnets which are described as Single Molecule Magnets (SMMs) when the details of their molecular structures are at atomic resolution. Other research interests are the synthesis of Super Metal Organic Frameworks (SMOFS) and the field of Biomimetics. The knowledge which can be won from these fields can be combined to lead to multifunctional materials, increased fundamental understanding of complex systems and a wide range of possible applications. This is the underlying research philosophy of the group. [1]

General scope

Multifunctional materials can only be discovered when cooperative effects operating within can be understood. At the heart of this endeavour is the aim to measure and understand the nature and mechanisms of cooperative effects in oxo-bridged coordination clusters (CCs) through applying a range of characterization methods. On one hand it will be possible to achieve a more fundamental understanding of the magnetic anisotropy in such systems, which is an essential condition for creating SMMs. On the other hand, there is the important aim of using new chemical syntheses and studying the resulting compounds by applying appropriate physical methods in order to search for new properties and open the way for producing multifunctional materials with a wide range of applications. [1]

In this thesis the term “oxo-bridged SMMs” refers to coordination clusters showing SMM properties in which the metal ions are held together by oxygen atoms deriving from various ligands or variously deprotonated protic solvent molecules. Such coordination clusters, as well as several examples of SMMs [2-5] built using ideas from supramolecular chemistry are structurally related to the basic concepts set-out by Alfred Werner in his Coordination Chemistry Theory. Just taking the example of a CC, in comparison with a coordination complex based on a single metal ion being held in a coordination sphere of lignands, the CC has a central collection of bridged and coupled (cooperating) metal ions encapsulated in a shell of ligands. For oxo-CCs the cooperativity is achieved by information transfer via the oxo groups. Overall, whereas a coordination complex will be a few Ångstroms across, a CC is usually more than 1 nm in cross-section. In a CC or Supramoelcular Coordination Compound (SCC) such as crown-ether complexes, the stabilizing and their influence on the properties are the same as in oxo bridged

CC being Molecular Magnets (MMs).[6-11] Non-covalent interactions in oxo-bridged MMs could be also of major importance for catalysis or other “hot” research areas today.[3,5] In particular CCs which are described as SMMs are realistic candidates for data storage applications.[12-13]

Subject

Normally, when chemists aim to synthesise Single Molecule Magnets (SMMs), they proceed according to the following steps: i) they probe ligands with possible selectivity for complexation of paramagnetic ions (often magnetically anisotropic) which later could lead to a cluster-compound with promising collective magnetism and where they think that this new compound might act as a SMM; ii) the structure of the new compound can be determined to atomic resolution (needs single crystals for X-ray diffraction) although it is mostly impossible to predict its SMM behaviour from the structure; iii) dc and ac magnetic measurements are used to characterise its collective magnetic and possible SMM behaviour ; iv) the discovered magnetic behaviour can be theoretically investigated as long as the system is not too big and thus can provide a benchmark for understanding later systems.[14] It should be noted that whilst it can be more instructive to work-out why a system does not show the desired properties (e.g. SMM behaviour) aimed for in the synthesis, it is generally true that very few of these “failures” are investigated further, which in turn means that often valuable insights are lost.

More than twenty years have passed since the discovery [14] that the Mn_{12}-ac coordination cluster originally reported by Lis [15] shows slow relaxation of magnetization. There have been extensive synthetic efforts aimed at adapting this system and the discovery of new SMM examples. However, very little systematic study has been carried out, so that in manganese CC chemistry only a few families of related CCs have been investigated. The Mn_{12}-system has, understandably, been the most toughly studied and a high number of compounds exist showing similar cores but with different ligands and sometimes different magnetic behaviour.[14] Other SMM families of 3d metal ions are those with the Mn_4[16], Mn_6[17] and Fe_4[18] coordination clusters.[14, 16-18] An enhancement of the energy barrier has been achieved within each family and it was also found that the exchange coupling as well as the ground spin state could be manipulated. However, in most of these cases the effect was related to a specific change in the overall structure influencing the collective magnetism. It was thus largely impossible to register whether any changes in the electronic nature of the encapsulating ligands can affect the overall magnetic behaviour for these systems. Indeed, in general any significant influence from making changes in the electronic donating or withdrawing effects of the ligands has been ignored, possibly as a result of the assumption that this would at most provide very minor perturbations.

Since all the above-mentioned cluster families contain only 3d ions, the assumption that the electronic properties of the ligands will not exert much influence on the resulting magnetism may well be valid since in general the coupling between 3d ions is relatively strong and can be expected to dominate the magnetic properties. However, recently chemists have turned their attention to synthesising CCs as possible SMM systems using lanthanides, mixtures of 3d and 4f ions and also a few examples of other blends of d and f ions such as 4d-4f. There are many examples such compounds from the Powell group with systematic work on 3d/4f systems used to discover the best sets of synthetic parameters needed to target specific types of SMM (see also *Fe/4f chemistry* and refs **[36]** later this chapter*)*. A special area of interest is in 3d/4f compounds where the 3d ion is Fe^{III}, which is an ion which not only produces fascinating SMM systems in 3d CC chemistry, but is also useful as a sensor for anisotropy in 3d/4f compounds via the information gained from using Mössbauer spectroscopy. This is a useful extra handle in this field since the highly anisotropic nature of lanthanide ions complicates the interpretation and understanding of magnetic measurements on these compounds. In general it is thought that the observed magnetic profiles are influenced by spin-orbit coupling to a greater extent than by the ligand field, although this is largely substantiated by studies on solid state compounds rather than the bounded CC systems which are becoming increasingly common. As will be seen in the following chapters of this thesis, a so-called “Paradigm shift” is needed in the description of CC systems incorporating lanthanide ions. The key features here are: i) the significant dipolar coupling effect between highly anisotropic lanthanide ions and between the 4f and 3d ions; ii) the interplay between strengths of super-exchange and dipolar coupling; iii) the significant input of both 3d metal ion and ligand on the overall electronic structure of the 3d/4f metal core and the overall anisotropy of the 4f ion. This third point suggests that in this context the more challenging task is actually to understand the effect of ligands, and maybe also the 3d ions, on the *f*-orbitals. **[19]**

For example, in this work a non-cyclic tetranuclear 3d/4f $\{Fe_2Ln_2\}$[20a] “test-bed” CC system was selected in order to investigate electronic nature of ligands on the magnetic anisotropy.[20b] See thesis overview.

1.2 Molecular Magnetism

History and basics

The phenomenon of magnetism was identified first in the mineral magnetite, which is a mixed valent inverse spinel compound which can be formulated as $\{Fe^{III}(Fe^{II}Fe^{III}O_4)\}$ or $(Fe^{II}O\text{-}Fe^{III}{}_2O_3)$ in order to emphasis its structural and magnetic features. [21] The relationship between magnetism and electricity was later made clear through the development of electromagnetic wave theory. [12, 21] In the 20th century Peter Weiss, developed the theory of ferromagnetism based on the assumption that the interaction between magnetic molecules could be described empirically considering an internal molecular field. Bohr identified the underlying physics from which magnetism results; i.e. the minute spin associated with an unpaired electron. This is the case in many solid state materials for which magnetic theory is mostly applied and discussed. The understanding of the magnetic behaviour of coordination compounds has been developed from the basic principles of the magnetism of bulk materials.[21]

In principle, every material interacts with a magnetic field with two basic types of behaviour: i) magnetism of single atoms or ions, namely diamagnetism and paramagnetism; ii) collective magnetism resulting from the cooperative coupling of centres in the material which can be classified as ferromagnetism, ferrimagnetism and antiferromagnetism. [21] In case the reader needs to refer further information about these basic principles, these can be found in standard textbooks. [21-25]

Since the discovery that Mn_{12}ac can show slow relaxation of magnetization and hysteresis as expected for bulk materials showing long-range ordering, but not for molecules, several other terms and definitions should be considered when discussing the SMM behaviour of CCs. In other words, how can we understand the observation that a single molecule responds to a magnetic field in the way we would expect for an ordered bulk solid? The important features such a molecule should possess for SMM behaviour to be observed are non-zero spin (usually as the ground state) combined with a sufficient degree of magnetic anisotropy to produce hard and easy axes of magnetization. A further feature important at this “Quantum World” level of scale (roughly nanoscale) is that quantum tunnelling (QTM – quantum tunnelling of magnetisation) can be expected and this can be regarded as undesirable if the goal is to store information or desirable if the goal is to process information (quantum computing). These aspects are discussed briefly below since they are important for the discussion of the results in this work, in particular in chapter 2.

Magnetic Anisotropy

A material is magnetically anisotropic when its magnetism becomes orientation dependent. While an isotropic material (in the absence of an applied field) has no preferential direction for its moment, an anisotropic system will align itself along an easy-axis (the energetically favourable direction of spontaneous magnetization). Two physical reasons are known to give rise to this anisotropy. These are dipolar effects (magnetic dipoles) and spin-orbital coupling. For example, in the case of an iron cylinder the cylindrical length is much greater than the circular diameter which means the magnetization will be oriented along its length to give an easy-axis. For an iron disk, the diameter is now the larger metric parameter and the direction of the length defines a hard axis. In the case of a spherical iron-ball, the system is isotropic as there is neither a favourable nor an unfavourable direction. This results from the inner crystallographic structure of the ball or the crystallographic anisotropy. Other forms of anisotropy are the magneto-crystalline anisotropy of the coupling of magnetization and crystal-cell (spin-orbital-coupling) and form-anisotropy which results from the changes in the form of a material. Finally exchange-bias or exchange-anisotropy which arises from the orientation of the magnetization in ferromagnetic materials is as a result of the interaction between it and an antiferromagnetic component.**[23,26]**

Quantum Tunnelling of Magnetization (QTM)

15 years ago two groups independently proposed an explanation for the unusual step-like features apparent in the magnetic hysteresis loops obtained from samples of Mn_{12}-ac.**[23, 26, 27]** Fig. 1.1.shows a schematic representation of the hysteresis behaviour of the Mn_{12}-ac SMM (measured at 2.1 K). The behaviour is not the result of thermal activation but caused through the loss of spin polarization in the molecules due to tunnelling of the magnetization through the energy barrier. **[23,27a)]**

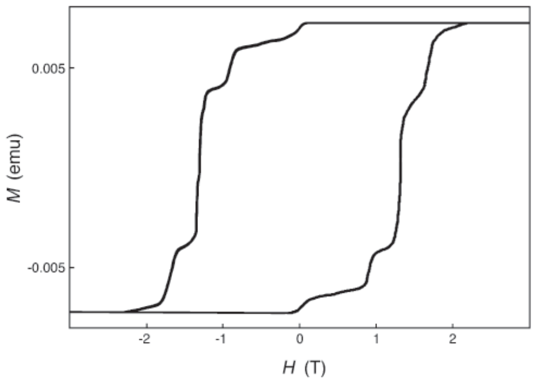

Figure 1.1. Schematic representation of the hysteresis of Mn_{12}-ac. The step-like curves represent the QTM in this compound.

Methods of measuring

For work on CCs in general and SMMs in particular the high sensitivity of the SQUID (Superconducting Quantum Interference Device) Magnetometer makes this the instrument of choice for measuring the magnetic behaviour and has been used in this work.**[28]** This method is based on the sensitivity the SQUID sensor (which is built from a weak Josephson-contact) on the change in the magnetic flux. Because a SQUID contains a superconductor, there is no electrical resistance at low temperature and thus no magnetic field. However, a circulating current can be induced by applying a field. This causes another magnetic field but in the opposite direction (Lenz-rule) according to the Meissner-Ochsenfeld effect. Theoretically, the BCS (Bardeen Cooper Schreiffer) theory which is about the Cooper-pair helps in understanding how a superconductor works in a SQUID.**[28]** Two types of SQUID magnetometers are useful, the *DC* and *AC* techniques. This combination in a SQUID is useful for identifying whether a material might be a SMM.**[29]** The DC measurement gives basic information about the overall magnetic behaviour as a function of temperature while the AC measurement is a more sensitive technique because a current field is applied from which one can determine the magnetic moment. In this case the induced moment sample is time dependent.

The *AC* measurement can give information about the magnetization dynamics **[29]** and it is possible to split the susceptibility χ and phase shift φ obtained from this measurement into a real part (in-phase, χ`) and imaginary part (out of phase, χ``). These two quantities are very important as aids in understanding SMM behaviour. It is possible to extract the energy barrier to spin inversion using an Arrhenius law analysis of the relaxation data (equ.1.1) and the blocking temperature to onset of slow relaxation of the magnetization can also be estimated from the data. The energy barrier and blocking temperature are related to each other (equ. 1.2). The magnetic measurement can take place at very low temperatures (He cooling) which is currently the temperature region where SMMs operate. The blocking temperature (T_B in K) is defined (according equ. 1.2) as the temperature below which the relaxation of the magnetization becomes slow compared to the time scale of a particular investigation technique. For example a molecule magnetized at 2 K will keep 40% of its magnetization after 2 months and by lowering the temperature to 1.5 K this will correspond to several years.

$$\tau = \tau_0 e^{(Ueff / k_B T)} \quad (1.1)$$

$$T_B = \frac{\Delta E = Ueff}{\ln(\tau / \tau_0) k_B} (1.2)$$

Where U_{eff} is the energy barrier to spin relaxation in cm^{-1} or K, τ_0 the relaxation time for the magnetization in a SMM and τ relaxation attempt frequency in s^{-1}.

Single Molecule Magnets

A Single Molecule Magnet (SMM) is a molecule that shows slow relaxation of the magnetization (magnetic bistability) of purely molecular origin. **[30]** These are coordination clusters which should show hysteresis of the magnetization at low enough temperatures with correct sweeping rates (Fig. 1.2). What can now be regarded as the “classical” criteria for SMM behaviour is a high spin ground state (S) and large negative axial-zero-field splitting parameter (D) to give an intrinsic energy barrier for spin reversal that results in slow relaxation of magnetization. In the meantime, with the study of systems incorporating metal ions which are much more anisotropic than ions such as the widely used high spin Mn^{III} ion, and with the observation that SMM behaviour can be observed in compounds where excited magnetic states are available, this definition needs some modification. An important point in dealing with highly anisotropic systems is that it is no longer possible to invoke a “giant spin” model to describe a collective, additive spin on the molecule (S) but instead the system is better described in terms of parameters which reflect the large contribution from orbital effects and the spin-orbit coupling. In this case, we can categorize a system showing SMM behaviour as one which possesses significant magnetic anisotropy and a non-zero spin state.

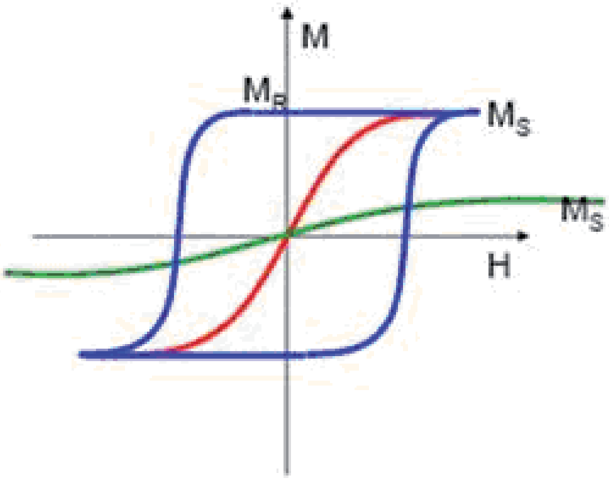

Figure 1.2. Schematic representation for the hysteresis: a ferromagnet or SMM (blue), superparamagnet (red) and paramagnet (green).

Theoretical reflection

Note that only the general equations in chapter 1 will have numbers. In all other chapters equations will not be numbered since they were used to for calculations and they are a part of the results discussion!

The general Hamiltonian which describes a magnetic system is given in equ. 1.3. H_0 is the unperturbed Hamiltonian. The Hamiltonian operator H_0 (equ. 1.3a) describes the two unperturbed potentials (Fig. 1.3) and treats the effect of an applied field parallel to the axis of the cluster and the axial-splitting through the crystal field. It can be expressed through the equations (1.3b) and the energy-levels of the sub-levels through equ. 1.4. H_1 describes the perturbation through the coupling of these two potentials (magnetization or/and applying an external magnetic field) and which leads to the degeneration of the M_s-levels (Fig. 1.3a, b). In addition, a third Hamiltonian H_2 describes the interaction with the surrounding. In Fig. 1.3 c) and is where the system relaxes and the two potentials are again equally occupied.[26, 30]

$$H = H_0 + H_1 + H_2 (1.3a)$$
$$H_0 = D[S^2{}_z - S(S+1)/3] + g\mu_B H_z S_z (1.3b)$$
$$H = D[S^2{}_z - S^2/3] + E[S^2{}_x + S^2{}_y](1.3c)$$
$$E(Ms) = D(M^2{}_s - 110/3) + g\mu_B H_z M_s (1.4)$$

D (negative for SMMs) is the axial and E is the rhombic zero-splitting parameter. The axial term of the Hamilton operator (which is an approximation) gives the energies of the M_s states, while the transversal terms the lead to mixing of the M_s states. This usually influences SMM behaviour negatively since QT becomes active. [26]

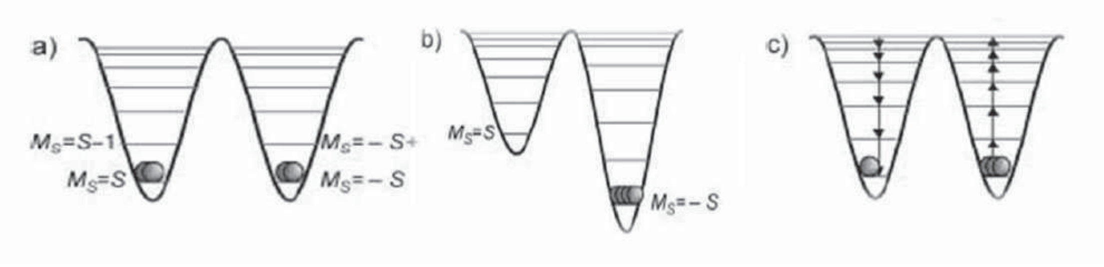

Figure 1.3. a) Undisturbed situation and D is negative so all ±M_s are in lowest states, b) disturbed through coupling, here also can the tunnelling happen and c) relaxation to the original state. [26]

Magnetic Properties of (oxo bridged) Fe^{III} in Complexes

A large ground spin state in CCs with Fe^{III} (d^5, high spin) could be achieved by assembling individual ions ferromagnetically. The high spin ground state of individual ions such as high spin Fe^{III} [31], Mn^{III} [32], Fe^{II} ($S = 2$) [33] is one reason why they are of interest in SMM research. In fact, all three ions can show significant single ion magnetic anisotropies, with the ZFS for the hs d^5 configuration of Fe^{III} resulting from mixing of low lying excited states. Iron(III) turns out to be a useful ion for producing SMMS.[31] A further relevant feature is that ferritin, the iron-storage protein form in most living organisms, can be considered itself as a nanosize magnetic particle. In fact ferritin has been investigated for quantum tunnelling effects of the magnetisation. Many large iron clusters have been reported, ranging from binuclear up to thirty nuclearity species. [31] All synthesized Fe^{III} SMMs so far reported are characterised by antiferromagnetic coupling between the Fe^{III} ions so that large spin in the ground state can only arise if the overall coupling can be described as ferrimagnetic.[read 31a)] Essentially such behaviour for a CC results from different magnitudes of exchange coupling between pairs of iron centres with a result similar to that seen in bulk ferromagnetic materials with antiferromagnetic coupling of spins of unequal magnitude (e.g. magnetite). In the molecular system the effect derives from the many different J-values present and which are responsible for the effect of uncompensated spin ground states. It has been argued that the defect Fe^{III} oxide maghemite, γ-Fe_2O_3 is an example of a bulk ferrimagnet with a similar type of non-compensation of magnetic moments and that ferrimagnetic iron–oxo clusters can be considered as models of this prototype mineral. [31a]

The exchange interactions in oxo-bridged Fe^{III} pairs have been much investigated both theoretically and experimentally. The simplest approach considers two parameters, the average metal–oxygen distance, P, and the metal–oxygen–metal angle, α. Magnetic data recorded on a large series of iron complexes suggest that the P-dependence of the exchange coupling constant, J, is well represented by equ.1.5.[31a]

$$J = 1.753 \times 10^{12} \exp(-12.663\,P)(1.5)$$

Where J (sometimes expressed as 2J) is expressed in cm^{-1}, P in Å, and the exchange Hamiltonian is in the form $H = JS1 \cdot S2$. The coupling constant is largely insensitive to the Fe–O–Fe angle for α > 120°. For smaller angles an effect is clearly observed, J becoming smaller as the angle α is reduced. A systematic study has been performed in a series of binuclear complexes with two alkoxo bridges and similar Fe–O distances. The values of the angles range from 102 to 106°, while J varies between *ca*. 15 and 21 cm^{-1}. Is the coupling constant negative? so the coupling is antiferromagnetic. The simplest correlation was found to be of the type given by equ. 1.6.

$$J = 1.48\alpha - 135\,(1.6)$$

With J being given in cm^{-1} and α in degree. An extrapolation of eqn. (1.6) suggests that for $\alpha \approx 90°$ the coupling should become ferromagnetic. The decrease in the antiferromagnetic coupling constant for α < 120° has been predicted by a complete exchange model recently. [31a, 34]

The anisotropy of the pairs depends on the anisotropy of the individual ions (single ion anisotropy) and on an additional term that is brought about by the interaction between the two iron ions (spin-spin anisotropy). High spin Fe^{III} has a d^5 configuration, which yields an orbital singlet ^6S ground term for the free ion. The ground state of the ion in complex is also orbitally non-degenerate; therefore the Zeeman anisotropy is very low, with $g_x \approx g_y \approx g_z \approx 2.0023$. However some admixture with excited states of lower spin multiplicity is allowed by spin–orbit coupling and the ground $S = 5/2$ state does show zero field splitting, which may easily be of the order of 1 cm^{-1}. [31a]

The anisotropy associated with the spin–spin interaction can be described to a good approximation by the interaction between the magnetic points dipoles centred on the two iron ions. For a pair of antiferromagnetically coupled ions the dipolar interaction orients the two spins orthogonal to the vector r connecting the two centres. In fact the poles of the same sign would be in contact for an orientation parallel to *r*. Therefore the plane perpendicular to *r* (Fig.1.4) is a hard plane for the magnetisation of the antiferromagnetic dimmer, which is more easily magnetised when the field is applied parallel to the axis connecting the two spins. **[31a]**

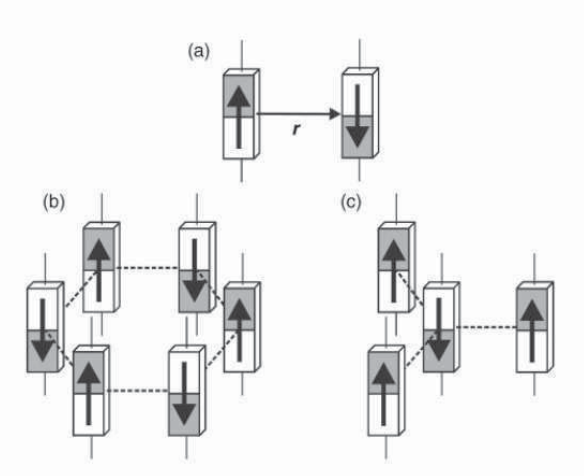

Figure 1.4. Schematic representation of preferred spin orientation due to the dipolar interaction in an antiferromagnetic Fe^{III} dimmer (a), in a cyclic antiferromagnetic Fe^{III} cluster (b), in a ferrimagnetic tetrameric Fe^{III} cluster (c). Adapted from **[31a)]**.

Dipolar interactions thus provide an Ising-type contribution to the magnetic anisotropy. These considerations can be extended to polynuclear systems. In particular, when antiferromagnetically coupled metal ions are arranged in a planar structure with axial symmetry, nearest-neighbour dipolar interactions determine an *XY* anisotropy with an easy plane of magnetisation when the ground state has $S = 0$ (Fig. 1(b)). In fact, in the lowest-energy configuration, the individual spins are antiparallel to their nearest neighbours (owing to exchange interactions) and perpendicular to the average plane through the metal array (dipolar interaction). **[31, 34]** A ferrimagnetic system, however, exhibits Ising type anisotropy (Fig. 1. c).

Cyclic CCs containing Fe^{III} which have so far been reported are six, eight, ten, twelve and eighteen member. In all the cases the Fe^{III}-Fe^{III} interaction is antiferromagnetic with S=0. Thus, the energies of the lowest states can be expressed according to equ. 1.7.**[31a]**

$$E(S) = J_{eff} S(S+1)(1.7)$$

Where J_{eff}= 4J/N, with N the number of iron ions. Such rings are non-magnetic at very low temperatures. By increasing the field the excited magnetic states are stabilized, till they become the ground state. Now the S=1 is the ground state and then S=2 and so on. This is result of energy state mixing such as in QT. [31, 34]

The smallest iron cluster (Fe^{III}) which found to exhibit slow relaxation of magnetization became in the meanwhile the first member of a family of $\{Fe_4\}$ clusters (Fig. 1.5, left). These compounds are ferrimagnets (S=5/2). [18, 31]

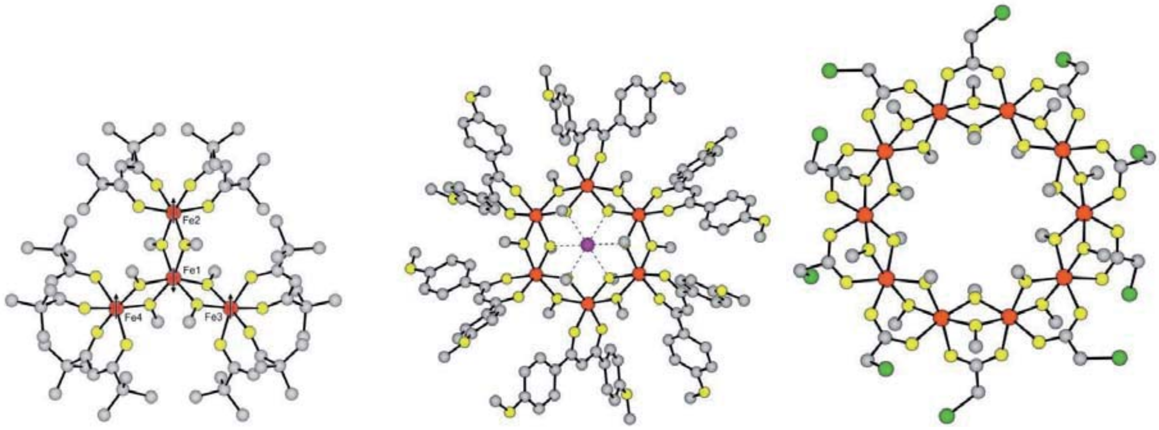

Figure 1.5. Examples: $[Fe_4(OMe)_6(dpm)_6]$ with dpm= 2,2,6,6-tetramethylheptane-3,5-dionate (left), $[NaFe_6(OMe)_{12}(pmdbm)_6]^+$ with pmdbm= 1,3-di(4-methoxyphenyl propane)-1,3-dionate (middle) and $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$ (right). Fe (red), O (yellow), Cl (green), Na (purple), C (grey). Adapted from [31a].

All members of this family are SMMs except one which has very similar parameters and was prepared with a Schiff-base ligand, which led to the question what makes a SMM?[18] A famous example of an Fe-SMM with high S is the $\{Fe_{19}\}$ S = 33/2 system.[31b-d)] Very recently, *Gatteschi et. al.* discussed and compared the properties of Molecular Nano-Magnets (MNM) and Magnetic Nano-Particles (MNP), using the Fe SMMs as examples of MNMs and postulating that these provide a bridge between the molecular and the bulk world of magnetism within a quantum regime. This gives hints as to how (if?) size can play a role in the magnetic properties of these two classes of compounds. [31l)]

Magnetic Properties of Ln^{III}

Strictly speaking, the lanthanides are the elements coming immediately after lanthanum in the periodic table where the 4f orbitals become filled with electrons. Lanthanum itself is part of group 3 (modern nomenclature) of the periodic table and sits directly below yttrium. Together with Sc and Ac these metals are known as the rare earths, although none of them are especially scarce. As a result of the size of its ionic radius, Y^{III} actually turns out to be a useful diamagnetic analogue for the later Ln^{III} ions which have substantially reduced ionic radii due to the lanthanide contraction. [19]

The energy levels of the $4f^n$-configurations can be derived using a Russell-Saunders coupling scheme to a fair approximation. Moreover, the spin-orbit coupling constants are very large (*ca.*1000cm^{-1}). As result, the lanthanide (few exceptions) ions feature a ground state with well defined value of total angular J with the result that the next J state is energetically much higher than k_BT (*ca.* 200 cm^{-1}) and consequently unoccupied. From there, the susceptibility and magnetic moments of lanthanides can be estimated using formulae with well-defined J values. In the case of Sm^{III} and Eu^{III} the first excited J-state is (as observed) close to the ground state. While anisotropic Ln^{III} ions are excellent candidates for obtaining SMMs, their electronic structures are extremely complex. [19]

This is because electronic spin is no longer the only significant source of angular momentum in the system. The degeneracy of the f orbitals yields large orbital moments (note Ho^{III} has the largest magnetic moment) that must be taken into consideration. Thus, for Dy^{III}, simply defining this as $4f^9$ is far less descriptive than the term symbol for the spin–orbit coupled ground state: $^6H_{15/2}$ (S = 5/2; L =5; J = 15/2) (Fig. 1.6, left). The spin–orbit coupled quantum number, J, is highly important since the spin–orbit coupling energy is generally larger than the effect of the crystal field for f-elements.

The ground J state of Dy^{III} is sixteen-fold degenerate ($2J_{Dy}$ + 1 states) and composed of magnetic sub-states, m_J, characterized by m_J= ±15/2,………, ±1/2 (+J, J-1, …-J). These projections of the total angular momentum quantum number can be affected differently by the surrounding crystal field, thereby removing the (2J + 1)-fold degeneracy of the ground state. This splitting, in combination with the strong spin–orbit interaction, links the orientation of the spin to the strength and symmetry of the ligand field. The implication for SMMs is that we can increase single-ion anisotropy simply by judiciously choosing the coordination environment of the lanthanide ion. It is becoming clear that the Dy^{III} ion often represents the ideal ion for single-molecule magnetism:[36a] it is a Kramer's ion, so a doubly degenerate m_J ground state must result, and it combines a large-moment $^6H_{15/2}$ ground state with significant anisotropy of the 4f shell.

Recently a perspective article from *Long et. al.*[19] was published. They give a simple model of the f-element electronic structure from which the single ion anisotropy of Ln^{III} ions is mainly discussed. They used the simplest Hamiltonian to describe the 4f ions plus their relation to the ligand field (equ. 1.8). They assume that single-ion anisotropy can be guaranteed when doubly generated m_J states can be largely separated from the excited ones through special ligand types such as the phthalocyanine ligands.

$$H = H_{ion} + H_{cf} \ (1.8)$$

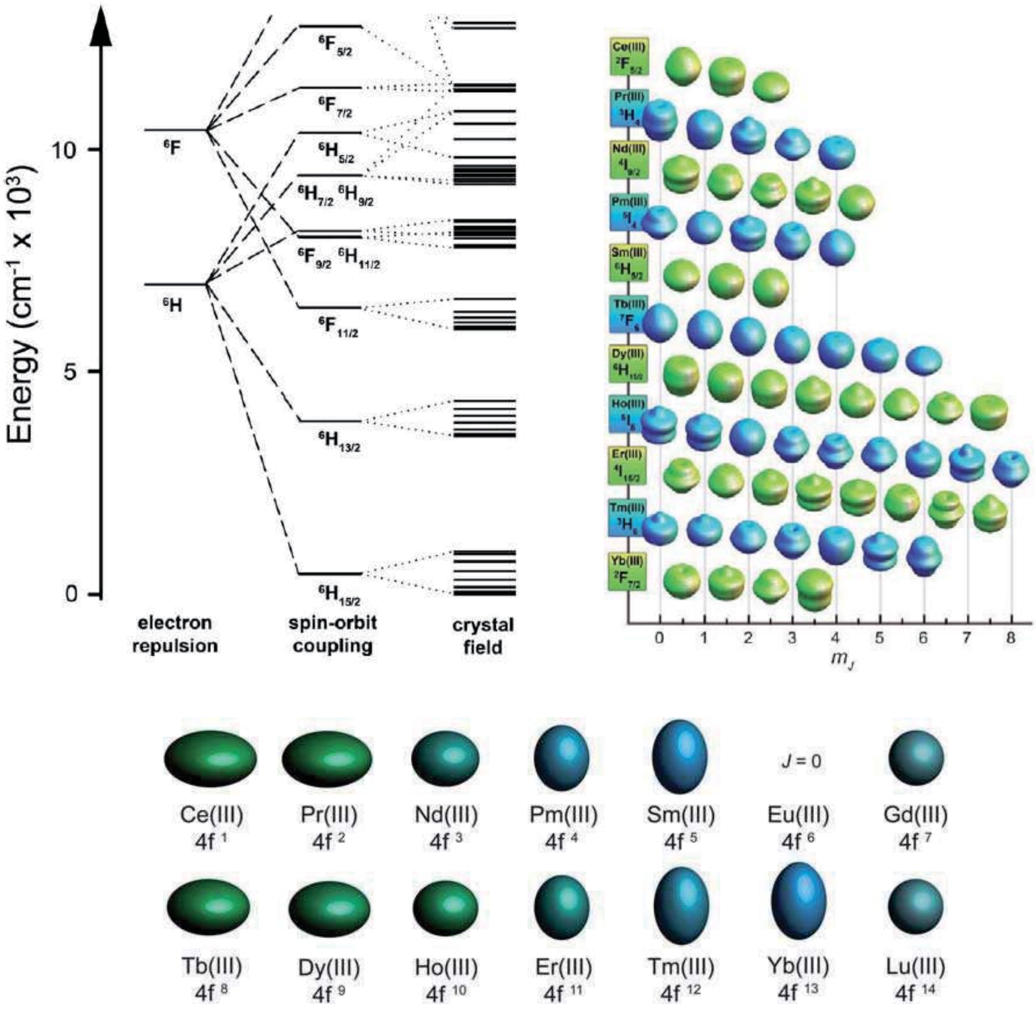

Figure 1.6. (Upper, Left) Low energy electronic structure of Dy^{III} ion with sequential pertubations of electron-electron repulsion (H_{ee}), spin-orbit coupling (H_{so}), and the crystal field (H_{lf}). The crystal field splitting is constructed from a model for the complex $[Dy((Me_3Si)_2N)_3]$. (Upper, Right) Approximation of the angular dependence of the total 4f charge density for m_J states composing the lowest spin-orbit (J) state for each Ln^{III}. In the absence of a crystals field all m_J states are degenerate. (Lower) the quadropule approximations fort he 4f shell distributions. Fore example, Tb^{III} oblate and Tm^{III} prolate. Prolate is axially elongated and oblate is equatorially expanded. Adapted from [19].

In Fig. 1.6 the electronic structure of the Dy^{III} ion (modelled for compound $[Dy((Me_3Si)_2N)_3]$) and the 4f charge density for the m_J states as well as the quadropule appromation for the 4f shell distribution for Ln^{III} ions are illustrated. These Figures are taken for the recently reviewed properties perspective article from *Long et. al.*[19]. They give a simple model of the f-element electronic structure from which the single ion anisotropy of Ln^{III} ions is mainly discussed. They discuss the shape of each ion's 4f-shell (the lowest *J*) (Fig. 1.7, upper and right and lower) as mathematically calculated quadruple approximations (Fig. 1.6, lower). They also discuss the angular dependence of the total 4f charge and how they differ for each ion (Fig. 1.6, upper and right).

However, this model also suggests a less explored method of generating strong single-ion anisotropy for single-molecule magnet synthesis involving strongly prolate ions like Tm^{III} and Yb^{III}. In general the Ln^{III} ions can provide remarkable examples of SMMs and SIMs showing very high energy barriers. [35] However, very fast relaxation rates and QTM effectively remove any possibility of using these high barriers to trap information in one magnetic sublevel state

Fe^{III}/4f chemistry

The strongest solid-state magnets are compounds containing lanthanides in conjunction with 3d metals such as $SmCo_5$ and $Nd_2Fe_{14}B$. In these materials, the electronic structure is usually described differently from the descriptions used for molecular systems and the link between the magnetic properties of CCs and such essentially inter metallic systems is hard to identify at present. However, the fact that such strong magnetism can be produced in these systems suggests that it should be possible to produce molecular-based systems with promising properties.

The number of FeDy SMMs is small and the work in our group is unique in exploring the synthesis of such compounds with the view to performing Magneto-Mössbauer correlation studies as a means of probing bulk and local propertiesFe/4f CCs based on molecular magnetism.[36] The clusters systems so far reported in the literature are: $\{Fe_2Ln_2\}$ (see chapter 2) [20], $\{Fe_5Ln_8\}$ [36b)], $\{Fe_7Dy_3\}$ [36c], $\{Fe_4Ln_2\}$ [36d)], $\{Fe_3Ln\}$[36e], $\{Fe_{16}Ln_4\}$ (see chapter 3) [36f] and $\{Fe_4Dy_4\}$[36g)] as well as $\{Fe_7Dy_4\}$[36h)]. Other groups reporting bulk magnetic studies on Fe/4f compounds have published data on $\{Fe_4Ln_2\}$ and $\{Fe_{12}Ln_4\}$.[37]

1.3 Magneto Caloric Effect (MCE)

3d-4f as well as 3d and 4f MMs are suitable candidates for showing the Magneto-Caloric Effect (MCE) if they possess high total spin. However, no MCE studies have been published so far on Fe/4f systems (see chapter 4). [38]

A thermodynamic interaction of a material with a magnetic field can cause an entropy change. The entropy (non-classical) of a system with a number of quantum states Ω (non-degenerated) is given in equ. 1.9. The relation between the entropy and magnetism can be found in the magnetic moment of a system since it has 2S+1 magnetic levels and this is given in equation 1.10.[39]

$$S_E = k_B \ln(\Omega) \quad (1.9)$$

$$S_E = R \ln(2S+1) \quad (1.10)$$

Fig. 1.7 shows the MCE with adiabatic demagnetization. The system is adiabatic which means that its entropy stays constant by changing the field. Now, if the system is adiabatic and it is in general state $A_i(T_i, H_i)$, also its temperature is T_i and “feels” a magnetic field H_i, and if the any change in the field would cause change in the entropy, so this change should be compensated somehow. In the MCE, the compensation can be by an equal but opposite entropy change associated to with lattice. As result of this the temperature of the system changes. [39]

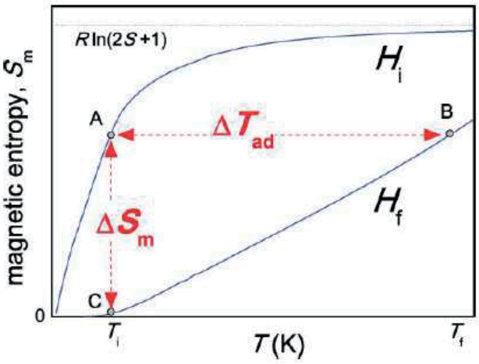

Figure 1.7. Molar magnetic entropy of a (super)paramagnet with spin S per formal unit, as a function of temperature, for magnetic field H_i and $H_f > H_i$. *AB* process: adiabatic magnetization providing ΔT_{ad}. *AC* process: isothermal magnetization providing ΔS_m. [39]

As shown in Fig. 1.7 the field change from *i* to *f* state brings the system to the general state B and the temperature of the material changes to T_f. The change in the entropy $\Delta S_{m.}$ can be achieved by the isothermal change of H_f which brings the system to the general state C. The MCE effect can be understood through the two characteristic parameters ΔT_{ad} and ΔS_m. [39]

Ferromagnetic materials become attracted to a magnet, thus, high spin compounds can show high MCE and particularly so if their spins are isotropically oriented.

This effect has been known since 1881 and is important in magnetic refrigeration; [40] in solid materials (e.g. containing Gd) [41] and in nano-materials [41]. However, only recently have chemists begun to investigate magnetic coordination clusters as systems which could allow access to extremely low temperatures. [38] It is very important to differentiate between the MCE effect for solid state materials and for CCs. *R. Sessoli et. al.* recently discussed this effect but for MM with the title “Chilling with Magnetic Molecules”. [39c)]

1.4 Mössbauer spectroscopy [42]

The Effect

The Mössbauer method will be discussed in more detail since this method is essential in the explanation of the magnetic behaviour of the compounds which are discussed in this work (mainly chapter 2 and 3).

The Mössbauer effect is based on the “recoil-free resonant nuclear-absorption” of gamma (γ) rays by a nucleus, which is emitted by their radioactive isotope source. Although many isotopes are theoretically Mössbauer-active; only a few are commonly investigated as a result of their long life-time and detectable ɣ-energy: ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{151}Eu.

The most used radioactive source is ^{57}Co , which decays via electron capture (EC, Fig.1.9) to the second excited state of ^{57}Fe (I= 5/2) with a γ-energy of 136 keV. 85-91% then relaxes to the first excited state of ^{57}Fe (I= 3/2) with 9-15% relaxing directly to the ground state ^{57}Fe (I= 1/2). In addition, a second relaxation can happen which is from the first excited state to the ground state and generates a γ-ray with energy 14.4 keV and which is used practically to investigate materials containing iron. The detector can be adjusted for the detection of this range of energy. All higher energy levels (such 136 keV) are too broad for detection and thus are subtracted.

To avoid loss of energy (kinetically) because of recoil the sample can be fixed in a matrix (crystal) such as a rhodium matrix which makes the atom massive enough not to recoil. In addition lowering the temperature of the measurement helps in minimizing the vibrations so that a good spectrum can be obtained. In these conditions it is possible to achieve resonant absorption by modulating the energy of the γ- ray beam by oscillating the γ- ray source with the resulting Doppler shift changing the energy of the photons (Fig. 1.10).

The Outputs

From Mössbauer spectrum three outputs can be later analyzed which give information regarding oxidation state, environment and magnetism of the studied matter (table 1.1): i) Isomer shift (δ), ii) Quadruple splitting (ΔE_Q) and iii) Magnetic splitting (ΔE_M). The isomer shift δ results from the difference in the electron densities around the nuclei on both sides (absorber and emitter). The spectra will be also shifted if the number of valence electrons in the absorber is different than that in emitter. This helps in identifying the oxidation state and the spin state. It can be expressed through the follow equation (equ. 1.11):

where, *Z* is the atomic charge, *e* the electronic charge, *R* effective nuclear radius, *c* velocity of light, E_γ energy of *γ*-ray, and $\rho(0)$ terms are total electron densities at the nuclei for absorber (a) and source (s). ΔR is the difference between *R* (excited) and R (ground).

$$\delta = \left(\frac{Ze^2R^2c}{5\varepsilon 0 E\gamma}\right)\left[\rho_a(0) - \rho_s(0)\right]\left[\frac{\Delta R}{R}\right] mms^{-1} \quad (1.11)$$

The 3d orbitals (here Fe; [Ar] $3d^6$ $4s^2$, Fe^{II}; $3d^6$ $4s^0$ and Fe^{III}; $3d^5$ $4s^0$) partially shields the nucleus from the influence of the 3s, and so the ion with the most electrons in the 3d orbital will do the most shielding, i.e. Fe^{2+}. This smaller density gives a greater magnitude of difference between the emitter and absorber, hence a larger isomer shift.

If the surroundings of the nucleus do not have spherically symmetric charge distribution, the nucleus will possess an electric nuclear quadruple moment. This leads to splitting of I= 3/2 to m_I= ± ½ and ± 3/2 (Fig 1.11).

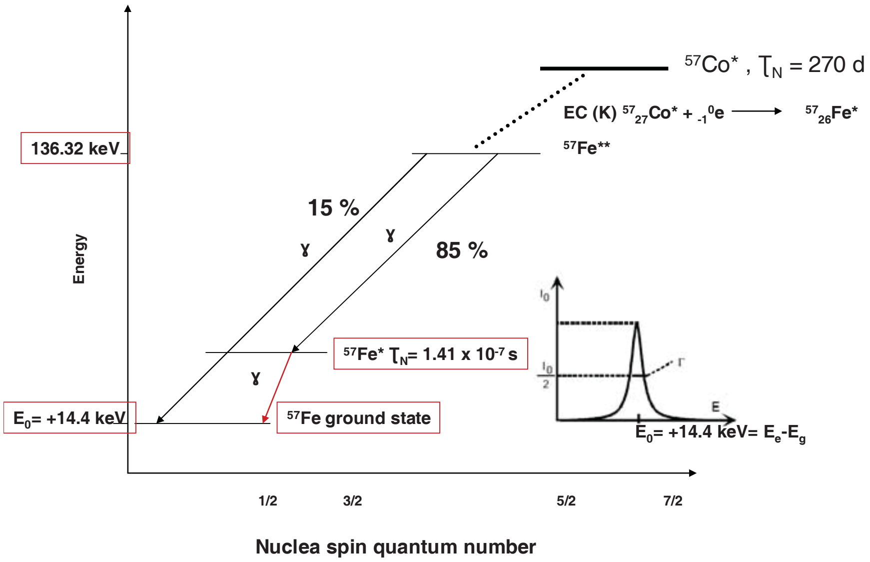

Figure 1.9. Shows a very trivial spectrum for an emitter and absorber in the same surroundings. [42]

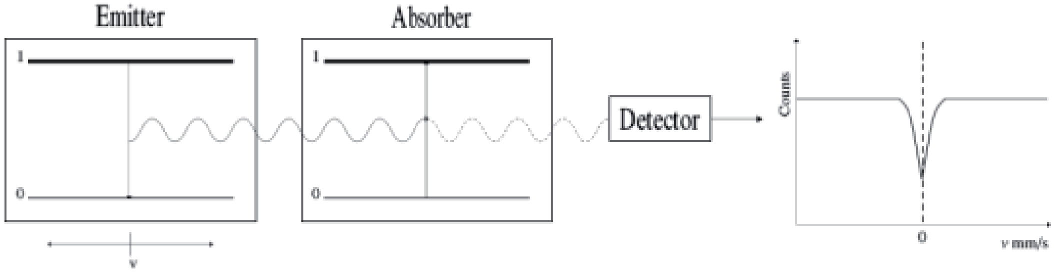

Figure 1.10. Singlet observed when Emitter and Absorber have same environment. [42]

The Spectrum

The splitting of the energy levels through a quadruple can be expressed through the formula (1.12): with the largest field gradient (equ. 1.13).

The angular dependency of the quadruple-term gives the possibility to determine the orientation of spins. The magnetic splitting is directly proportional to the applied magnetic field. In this case the nucleus interacts with the magnetic field and this leads to removing the degeneracy of the sub-states with angular momentum quantum number (I> 0 to 2I+1). The ground state of ^{57}Fe splits into two (-1/2 and 1/2 and the first excited into four (-1/2, +1/2, -3/2, and 3/2). The allowed selection rule is that $\Delta m_I = 0, \pm 1$ and there are thus six maximum obtainable transitions. (Fig. 1.12)

Table 1. 1. Summary of the information which can be gained from Mössbauer measurements.[43]

Interaction	Mössbauer-parameter	Informations
electric monopol-interaction between nuclei and the electrons at nuclei sites.	Isomer shift δ [mm/s]	-oxidations state - bonds - electro-negativity of ligands - spin state
electric quadruple- interaction between electric quadruple moment of a nuclei and inhomogeneous electric field at nuclei sites.	Quadruple splitting ΔE_Q [mm/s]	- molecule symmetry - bonds
magnetic dipole- interaction between magnetic dipole moment of nuclei and magnetic field at nuclei sites.	Internal magnetic splitting ΔE_M [mm/s]	- magnetism of material

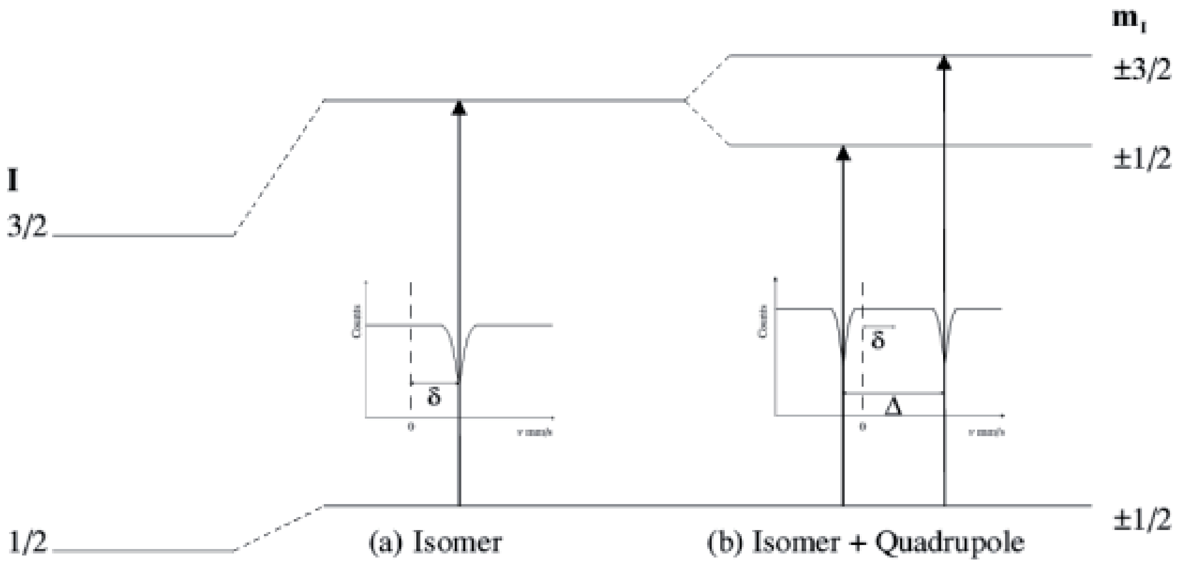

Figure 1.11. Schematic representation of isomer and quadruple splitting to $m_I = \pm 1/2$ and $m_I = \pm 3/2$. [42]

$$\Delta E_Q = eQV_{zz} \quad (1.12)$$

$$V_{zz} = \frac{1}{4\pi\varepsilon_0} \sum_i q_i^{-3} (3\cos^2\theta_i - 1) \quad (1.13)$$