Introduction:

Magnets are a multi-billion dollar annual industry with a cloud of uses such as in switches, computer hard drives, credit/debit/ATM cards, televisions, audio devices, motors, and highly specialized instruments such as medical MRI equipment, among many others.[1] The need for smaller and smaller magnets progressively increases as industry continues the push towards greater miniaturization, smaller devices, and more digital information storage in a computer hard drive or iPod memory, the need for smaller and smaller magnets increases. Magnetism has consequently become a major sub-division of Nanoscience. The need is for nanoscale magnets of identical size and behaviour, and the standard approach to this has been to make smaller and smaller pieces of traditional magnets, which are composed of metals, metal alloys, metal oxides, or similar. This so-called ‘top-down’ approach is reaching its limits as the ability to fabricate nanoscale magnets that are of identical size (i.e. monodisperse) becomes increasingly more difficult with decreasing size.

Fig.1.1: Several examples of SMMs depicted together and compared to the superparamagnetic nanoparticle.[2]
Progressive research over the last decade in the inorganic chemistry community has allowed the synthesis of an exciting class of materials with unique magnetic properties.[3] These new materials were given the name “single molecule magnets” (SMMs) for reason that the ability of a single molecule to function as a magnet. The ability of a single molecule to behave like a bulk magnet caught the attention of researchers because such systems may lead to the smallest possible magnetic devices.[4]

Thus the magnetic functioning of a single molecule is of great importance to the field of nanomagnetism because it represents an alternative, ‘bottom-up’[5] route (from atomic to molecular level) to nanoscale magnetic materials. Also, it brings to the area all the advantages of molecular chemistry, including monodispersity, crystallinity, true solubility (rather than colloid formation), protection by a shell of organic groups that prevents close contact of a molecule’s magnetic core with those of neighboring molecules, and the ability to vary this organic shell at will using standard chemical methods.[1] Such molecules are called single-molecule magnets (SMMs).[6–9] They have also occasionally been called molecular nanomagnets. A few examples are shown in the gallery of single molecular magnets as below:
The importance of SMMs is that their molecules display properties intermediate between those of simple paramagnets in the mesoscopic regime and the classical bulk magnets in the macroscopic regimes. These molecules are of nanoscale dimension, with magnetic moments that range from a few atomic spins to a few hundred spins. Their intermolecular exchange interactions are rather weak and there is no long-range ordering.
Fig. 1.2: Gallery of single molecular magnets: (a) Mn$_{12}$ (b) ferric star (FeFe$_5$L$_6$) (c) [2X2]-grid (d) ferric wheel (CsFe$_8$) (e) Mn$_{19}$ (f) Fe$_8$ (g) Mn$_{84}$ (h) Mn-Ni-Mn SCM, (i) Mn$_{18}$. [1,6,9,10]

The importance of SMMs is that these molecules show properties intermediate between those of simple paramagnets in microscopic regime and the classical bulk magnets in the macroscopic scales. These molecules are of nanoscale dimensions ~ 1.5 nm in diameter and they represent the point at which the classical and quantum worlds meet because they are macroscopic entities which display quantum effects.[11]

All SMMs have transition metal ions such as Fe, Mn, Ni and Co as the source of their magnetic properties. The magnetic core of each complex comprises multiple ions with unpaired electrons, which are strongly coupled to each other through intramolecular exchange interactions. Intramolecular exchange is the interaction between the ions within a molecule, and the bulky organic ligands that surround the magnetic core serve to isolate each molecule from surrounding neighbors. Thus, intramolecular exchange interactions are rather weak and there is no long range ordering.
This isotropic Heisenberg exchange interaction is expressed as

\[ \hat{H}_{\text{isotropic}} = \sum_i \sum_{j \neq i} J_{ij} \hat{S}_i \cdot \hat{S}_j \]

In the above eq., \( J_{ij} \) is the magnitudes of the isotropic Heisenberg interaction between spin \( i \) and spin \( j \) (positive for antiferromagnetic coupling and negative for ferromagnetic coupling). \( S \) represents the spin operator for an individual ion within the molecule. This coupling leads to a large magnetic moment for each molecule, and separates the energy spectrum into respective spin multiplets.

Fig. 1: \( M_s \) quantum number corresponds to \( 2S+1 \) orientations (left) and energy spectrum of these \( M_s \) states (right).

Each molecule can be considered as an independent magnetic nanocluster possessing a large magnetic moment. Since each molecule behaves like an isolated magnetic moment, the term single molecule magnet was appropriately coined for such compounds.
Origin of Single Molecular Magnetism:

Magnetism observed in a single molecule has different origin than that of the classical magnetism.[12] SMMs are nano clusters in which each molecular unit can contain as few as two and up to several dozens of paramagnetic ions (spins). A single molecular magnet has an appreciable potential barrier for reversal of the direction of magnetization. In other words, if the magnetic moments of individual molecules in a crystal of a SMM are aligned parallel to an external field, the temperature is lowered, and the field removed, the SMM would remain magnetized with parallel spins at low temperatures. There are two basic requirements in order for a molecule to function as SMM. First, the ground state of the molecule should have a large spin S. Second, there need to be considerable negative anisotropy present.[13]

Main Features of Single Molecular Magnets:

To function as an SMM, a molecule must display slow magnetization relaxation below a characteristic blocking temperature, $T_B$. This behaviour is shown as a result from a large ground spin state (S) (i.e., lots of unpaired electrons) combined with a large and negative Ising (or easy-axis) type of magneto-anisotropy as measured by the axial zero-field splitting (zfs) parameter, D. This combination leads to a significant barrier to magnetization reversal, whose upper limit ($\Delta E$) is given by $S^2|D|$ or $(S^2 - 1/4)|D|$ for integer and half-integer spins, respectively.[1]

The slow relaxation in the magnetization is due to the presence of an energy barrier which has to be overcome in the reversal of the magnetic moment. This behaviour has been compared to that of super paramagnetic materials. Super paramagnetic behaviour occurs when a single magnetically ordered domain has a reorientation barrier that is comparable to the thermal energy.[15] As a consequence, the magnetization flips freely and its time average is zero, as in a paramagnet. In an external field, it behaves like a paramagnet until the temperature is sufficiently reduced such that the barrier cannot be easily overcome. Thus the magnetization is
blocked, below a blocking temperature, $T_B$, and the super paramagnet reverts to its usual bulk behaviour (i.e. ferro-, ferri-, or antiferromagnetic).

![Diagram](image)

Fig. 14: The energy barrier for a molecule of Mn$_{12}$Ac in zero field.

The axial anisotropy forces the magnetic moment to point either parallel ("up") or antiparallel ("down") to the quantization (easy) axis. The energy barrier to magnetization reversal is given by $|D|S^2$.

The number of spin projections (energy states) for any molecule is given by $2S + 1$, where $S$ is the spin ground state of the molecule. In the absence of any transverse anisotropies or transverse fields, energy states with equal but opposite spin projections are degenerate in zero magnetic field. The energy eigenvalues for each eigenstate:

$$E(m_s) = D m_s^2$$

where $m_s$ is the spin projection along the $z$ axis. The ground state for the system is the largest magnitude of the spin projection ($m_s = \pm S$), since $D$ is negative.

This axial anisotropy allows one to define a quantization axis, (generally the $z$ axis) for the energy levels of the system, which are quantized. The energy barrier makes the
magnetic moment bi-stable due to the fact that energetically it prefers to point in one direction (+z) or a direction that is antiparallel to the first (−z).

This anisotropy occurs in the absence of an external magnetic field. Another phenomenon occurring in the absence of any external field is known as zero field splitting. However, anisotropies can manifest themselves in the presence of an external field as well, in terms of the Zeeman interaction. In an external magnetic field, the Zeeman energy of an electron now depends on the orientation of the field with respect to its spin projection along the field. The energy of the Zeeman interaction is related to the strength of the external magnetic field by a proportionality factor, \( g \). Eq. gives the general expression for the Zeeman energy:

\[
E_{\text{Zeeman}} = \mu_B B \cdot g \cdot S
\]

where \( \mu_B \) is the Bohr magneton, \( B \) is the external field strength, \( g \) is the Landé tensor and \( S \) is the spin operator for the molecule. For a free electron \( g \) is a scalar (≈ 2), but in a molecule \( g \) becomes a tensor due to spin–orbit induced anisotropies.

The zero field mechanism manifests itself in the lifting of degeneracies of energy levels through energy splitting.[3] Zero-field splitting causes magnetic anisotropy, and has profound effects on magnetic properties. For example, magnetic hardness (≈ the width of a hysteresis loop) is related to the magnetoanisotropy.

An SMM exhibits the super paramagnet like properties, displaying both a frequency-dependent out-of-phase ac magnetic susceptibility signal, and hysteresis in a plot of magnetization versus applied dc magnetic field; these are both classical properties of magnetic materials.
Fig.1.5: In-phase and out-of-phase AC susceptibility signals.

AC susceptibility studies at several oscillation frequencies can be used as a means of determining the true or effective energy barrier ($U_{\text{eff}}$) to magnetization relaxation, because at the $\chi''$ peak maximum the magnetization relaxation rate ($1/\tau$, where $\tau$ is the relaxation time) is equal to the angular frequency ($2\pi \nu$) of the oscillating ac field. Hence, out-of-phase ac measurements at different oscillation frequencies are a valuable source of relaxation rate vs. $T$ kinetic data that can be fit to the Arrhenius equation,

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp \left( \frac{-U_{\text{eff}}}{kT} \right)$$

Or

$$\ln \left( \frac{1}{\tau} \right) = \ln \left( \frac{1}{\tau_0} \right) - \frac{U_{\text{eff}}}{kT}$$

For the magnetization in a SMM, the relaxation time is expected to follow this Arrhenius equation.

Fig.1.6: Plot of the natural logarithm of the magnetization relaxation rate versus $1/T$ for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^1)_1\text{OD}(\text{C}_5\text{H}_{11}\text{OH})_2]$. 

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In addition, they not only display classical properties but also quantum properties such as quantum tunneling of the magnetization vector (QTM) through the barrier. The distinctive property of SMMs is the occurrence of magnetic hysteresis at low temperature so that each molecule behaves as a tiny magnet. One additional feature of SMMs is the occurrence of "steps" in their hysteresis loop. Such steps reflect the availability of quantum-mechanical "shortcuts" for the reversal of the magnetic moment. The steps, which are an indication of the phenomenon of MQT, occur when the \( m_s \) levels on each side of the classical barrier become degenerate as a result of the applied magnetic field, and the magnetization vector can tunnel across.

![Magnetic hysteresis loop of SMM (Mn_{12}-ac).](image)

**Fig. 1.7:** Magnetic hysteresis loop of SMM (Mn_{12}-ac).

Magnetic quantum tunneling (MQT) is defined as the tunneling of the magnetization vector from a level on one side of the classical energy barrier to a level on the other side. Phonon assisted MQT occurs when the magnetization vector is excited to a higher energy \( m_s \) level and then tunnels through the barrier. For all these reasons, SMMs have been proposed for various specialized applications, such as ultra-high density memory devices, spintronics, and quantum computing.
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Fig. 1.8: Schematic of the degenerate $m_s$ levels in zero magnetic field, separated by the classical barrier.

Magnetic Anisotropy:

Anisotropy plays a fundamental role in the magnetic properties of all SMM systems. Since they comprise multiple transition metal ions, SMMs constitute an exchange coupled system. The anisotropy can come from many sources, including spin-spin dipolar and exchange coupling of electrons, hyperfine interactions of electrons with the nuclei of the constituent atoms of the molecule, and most notably spin orbit coupling of the electrons. All of these sources can lead to anisotropic electron distributions on the molecule. This coupling is responsible for the essential feature of SMMs, which is their negative axial anisotropy that creates a barrier to magnetization reversal.

Spin orbit coupling results from the interaction of one electron’s orbital angular momentum with its own spin angular momentum.[3] The orbital momentum of an electron creates a magnetic field, which will couple to the spin magnetic moment. This type of coupling is also present between the spin of the electron and the magnetic field of a proton, which constitutes an orbital momentum.
One source of anisotropy is the Jahn-Teller elongations of electronic orbitals. Such a distortion of molecular orbitals of the Mn$^{3+}$ ions is the significant contribution to the axial anisotropy in the Mn$_{12}$Ac SMM system. The Jahn-Teller theorem states that "for a non-linear molecule in an electronically degenerate state, a distortion must occur to lower the symmetry, to remove the degeneracy, and lower the energy."

An atom in free space with a symmetric distribution of electronic orbitals will have no anisotropy and therefore, the energy levels of a certain orbital will be degenerate. But atoms in a molecule will have their molecular orbitals distorted. This distortion can be a geometric compression or elongation and it causes degeneracies to be lifted. In the case of a compression, the sign of the axial anisotropy parameter, D, is positive and conversely, D is negative in the case of an elongation.[3] If the distortion occurs along one axis only, then only axial anisotropies will develop. If the distortion occurs along multiple axes, then both axial and transverse anisotropies will develop.

Spin-spin dipolar coupling between electrons arises from the interaction of one electron's spin with another electron's dipolar field. Similar interactions between electrons and nuclei can give rise to hyperfine couplings. The nuclei in most materials have magnetic moments which couple to the orbital and spin angular momentum of the electrons. However, in exchange coupled systems, like SMMs, the delocalization of electrons throughout the molecule usually makes this a weak effect. Although, the interactions between a molecule and the fields from nuclear moments as well as other molecules play an important role in the tunneling process.[4]
Magnetic Hysteresis and Magnetic Quantum Tunneling:

In the absence of any transverse anisotropies or transverse fields, energy states with equal but opposite spin projections are degenerate in zero magnetic field. When an external magnetic field is applied, it shifts the energy levels of the potential well with respect to one another. At low temperatures \( kT < D \) where only the ground state of a molecule is significantly populated, we can observe magnetic hysteresis. Many studies have been done reporting magnetic hysteresis loops in various systems.[1]

In SMM systems, it is the anisotropy barrier of each individual molecule that is responsible for the observed hysteresis. At low temperatures, the anisotropy barrier makes it energetically favorable for all the spins to populate the ground state of the system. The barrier prevents spins from directly reversing their spin state projection from parallel to antiparallel with respect to the quantization axis.

Most interesting is the appearance of steps in the hysteresis loops, which is an indication of quantum tunneling of the magnetic moment through the anisotropy barrier. At resonance fields, the magnetization is seen to have steps where it moves toward the opposite saturation value. This indicates that spins are reversing their projection state by tunneling through the energy barrier at these resonance fields.

Future Applications:

One of the most pressing technology needs today is to find more efficient ways to store and process digital information. Very important possibilities are:

- To squeeze more and more data onto storage devices.
- To develop fundamentally different ways to process information, such as quantum based computing.

For any of these potential applications, the use of chemistry has developed new materials, known as single molecular magnets.
We have many types of magnets today made from iron, cobalt and nickel, metal alloys, and metal oxides. They are already fantastic. But single molecules are much smaller than even the smallest magnetic particles, and if a molecule can function as a magnet, then we can use a molecule to store information—one bit of information per molecule.

The smallest metal nanoparticles used in research are about 3 nm in diameter, which contains near about 1000 atoms. The most information that can be stored on hard drives and other devices currently used is 3 billion bits (or 3 gigabits) in 1 cm² area of a cobalt-based magnetic material. The much smaller size of our molecules means we could get 30 trillion bits of them into 1 cm² and thus a storage density of 30 trillion bits (or 30 terabits) is feasible. This is 10,000 times greater than the current best by computer manufacturers. Regardless of whether or not the realization of these applications is ever achieved, SMMs are interesting to study from a purely scientific aspect. [3]

Although complexes displaying SMM behaviour are known for several metals, manganese cluster chemistry containing at least some Mn^{10} atoms has been the most fruitful area to date. [20, 21] Using only a limited assortment of ligands and starting materials, cluster products with a wide range of Mn uncertainties can be obtained, with a taking almost all values up to 50, plus Mn_{25}, Mn_{26}, Mn_{27}, and Mn_{28}, the latter being the largest to date. [20] Mn_{29} will be the only molecules discussed in this thesis, and I have included the various Mn_{13} SMMs with their structural and other related information.

In Mn_{13} SMMs consists of [Mn_{13}O_{25}] core. This manganese oxide core is composed of the Mn^{10}O_{12} cube surrounded by a ring of 8 Mn^{11} units connected through bridging oxo ligands. The common feature of SMMs responsible for their interesting behavior is the strong spin-spin coupling between metallic ions in the core of the molecule. For instance, in Mn_{13}, there are 4 Mn^{11} molecules (spin 5/2) surrounded by 8 Mn^{10} atoms.
Background on Molecular Magnets:

The Early Types of molecule-based magnets, first developed in the late 1960s, consist of three dimensional arrays of inorganic or organic molecules, particularly organometallic complexes. In these compounds, some of which are magnets at room temperature, the magnetism arises from the collective unpaired electrons of the bulk material, similar to iron or cobalt metal particles. A lot of progress has been made on developing these 3-D based magnets since the late 1980s.

Firstly, Lis synthesized [Mn_{12}O_{12}(O_2CMe)_16(H_2O)_4].2MeCO_2H.4H_2O (called Mn_{12}-aceta...ne) and received little attention until its magnetic bi-stability was realized.[19] This discovery initiated the field of molecular nanomagnetism. The term “single molecule magnet” was first employed by David Hendrickson, a chemist at the University of California, San Diego and George Christou (Indiana University) in 1996.

Although complexes displaying SMM behaviour are known for several metals, manganese cluster chemistry containing at least some Mn^{III} atoms has been the most fruitful source to date.[20,21] Using only a limited assortment of ligands and starting materials, cluster products with a wide range of Mn_{x} nuclearities can be obtained, with x taking almost all values up to 30, plus Mn_{32}, Mn_{46}, Mn_{70} and Mn_{84}, the latter being the largest to date.[20] Mn_{12} will be the only molecules discussed in this thesis, and I have included the various Mn_{12} SMMs with their structural and other related phenomenon.

All Mn_{12} SMMs consists of [Mn_{12}O_{12}] core. This manganese oxide core is composed of Mn^{IV}_4O_4 cube surrounded by a ring of 8 Mn^{III} units connected through bridging oxo ligands. The common feature of SMMs responsible for their interesting behavior is the strong spin-spin coupling between metallic ions in the core of the molecule. For instance, in Mn_{12}, there are 4 Mn^{4+} molecules (spin 3/2) surrounded by 8 Mn^{3+} atoms
(spin 2), and it has been determined [22] that they retain a relative orientation such as
to give the whole molecule a spin of 10 (= 8(2) – 4(3/2)). This calculation can be
summarized in the following manner:

\[
\text{Mn}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 \\
S = 4/2 = 2 \\
8\text{Mn}^{3+} = 8 * 2 = 16 \\
\text{Mn}^{4+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 \\
S = 3/2 \\
4\text{Mn}^{4+} = 4 * 3/2 = 6
\]

.: Spin State of \([\text{Mn}_{12}O_{12}(O_2CR)_{16}(H_2O)_n]\) complex = 16-6 = 10

The four central Mn^{IV} atoms are weakly ferromagnetically coupled and the remaining
Mn^{III-Mn}^{IV} and Mn^{III-Mn}^{III} interactions are all antiferromagnetic, with the former much
stronger than the latter, as expected on the basis of literature data.[23] As a result, the
stronger Mn^{III-Mn}^{IV} interactions overcome the weaker Mn^{III-Mn}^{III} ones within each
triangular Mn^{III-Mn}^{IV} sub-fragment of the core, aligning the spins of the outer Mn^{III}
atoms all parallel, and thus antiparallel to the central Mn^{IV} atoms.

Fig.1.9: \([\text{Mn}_{12}O_{12}]\) core of Mn_{12} complexes that gives their S = 10 ground states.
Colour scheme: Mn^{IV} green, Mn^{III} blue, O red.
Objective of the present work:

Single-molecule magnets (SMMs) are individual molecules that can function as nanoscale magnetic particles. The $[\text{Mn}_{12}\text{O}_{12} (\text{O}_2\text{CR})_{16} (\text{H}_2\text{O})_4] (\text{Mn}_{12}; R = \text{Me}, \text{Et}, \text{etc.})$ family of SMMs was the first one discovered; it is also the one whose study has provided the majority of current knowledge on this interesting magnetic magnets. The present work is to write a review on single molecular magnets that will survey the various chemical studies that have been carried out phenomenon. My objective of the present work is to review the single molecular magnets mainly manganese clusters up till now. This will include a discussion of methods that have been developed for their magnetic and SMM properties.