Chapter 4

Magnetoochemistry of Single Molecular Magnets

In this chapter, we have discussed various phenomena related to Single Molecular Magnets with their graphical illustration which have been categorized as follows:

- DC Magnetic Susceptibility Studies
- AC Magnetic Susceptibility Studies
- Magnetic Hysteresis and Quantum Tunneling of Magnetization

DC magnetic susceptibility studies:

The spin alignments (parallel/antiparallel) have been directly confirmed on a single crystal of \( \text{Mn}_{2}\text{O}_{2}\text{O} \cdot \text{H}_{2}\text{O} \cdot 2\text{MeCO}_{2}\text{H} \cdot 4\text{H}_{2}\text{O} \). Similarly, the significant D value is primarily due to the near-parallel alignment of the eight Mn\(^{\text{II}}\) JT axes (Fig. 12). Each JT distortion results in significant single-ion anisotropy for Mn\(^{\text{III}}\), whereas Mn\(^{\text{II}}\) and Mn\(^{\text{III}}\) are relatively isotropic. Thus, the near-parallel alignment of eight Mn\(^{\text{II}}\) JT axes leads to a significant molecular anisotropy (D value) because the latter is the

\[ 55 \]
Chapter-4

Magnetismochemistry of Single Molecular Magnets

In this chapter, we have discussed the various phenomenon related to Single Molecular Magnets with their graphical illustration which have been categorised as follows:

- DC Magnetic Susceptibility Studies
- AC Magnetic Susceptibility Studies
- Magnetic Hysteresis and Quantum Tunneling of Magnetization

DC magnetic susceptibility studies:

Variable-temperature magnetism studies have established that the Mn\textsubscript{12} complexes possess $S = 10$ ground states and $D = -0.5 \text{ cm}^{-1}$. The significant value of $S$ can readily be rationalized on the basis of the sign and relative magnitude of the exchange interactions within the Mn\textsubscript{12} core, with adjustments to reproduce the bulk magnetization data. [31]

The spin alignments (parallel/antiparallel) have been directly confirmed on a single crystal of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4].2\text{MeCO}_2\text{H}.4\text{H}_2\text{O}$. [31] Similarly, the significant $D$ value is primarily due to the near-parallel alignment of the eight Mn$^{\text{III}}$ JT axes (Fig. 1); each JT distortion results in significant single-ion anisotropy for Mn$^{\text{III}}$, whereas Mn$^{\text{IV}}$ and Mn$^{\text{II}}$ are relatively isotropic. Thus, the near-parallel alignment of eight Mn$^{\text{III}}$ JT axes leads to a significant molecular anisotropy ($D$ value) because the latter is the tensor sum of single-ion anisotropies. [1]
Fig. 4.1: The thicker black bonds indicate the positions of the Mn$^{III}$ Jahn–Teller elongation axes. Colour scheme: Mn$^{IV}$ green, Mn$^{III}$ blue, O red, C grey.

A representative plot of the magnetization (M) data for a sample of SMM collected at various fields (H) and different temperatures (generally low) is, plotted as M/NμB vs. H/T (N is Avogadro’s constant, μB is the Bohr magneton) as shown below.

Fig. 4.2: Isofield plots of reduced magnetization (M/NμB) vs. H/T for microcrystalline Mn$_{12}$-acetate at the indicated fields. The solid lines show the single fit.
For complexes populating only the ground state and possessing no axial zfs (D = 0), the isofield lines would all superimpose and saturate at a value of gS. If the data clearly do not superimpose, it indicates a significant D value. The nonsuperimposition of the isofield lines clearly indicates the presence of ZFS.

The data can be fit by diagonalization of the spin Hamiltonian matrix, assuming that only the ground state is populated at these temperatures (a valid assumption for normal Mn\textsubscript{12} complexes), incorporating axial zfs \((D \hat{S}^2)\) and the Zeeman term, and employing a full powder average.[52] The corresponding spin Hamiltonian \((\mathcal{H})\) is given by the following equation,

\[
\mathcal{H} = D \hat{S}_z^2 + g \mu_B \hat{S} \cdot \mathbf{H}
\]

where \(\hat{S}_z\) is the z-axis (the easy-axis for Mn\textsubscript{12}) spin operator; the last term is the Zeeman energy associated with the applied field \(H\). The best fit is shown as the solid lines in Fig.4.2, and the fit parameters in this case were \(S = 10, D = -0.50\ \text{cm}^{-1}\), and \(g = 2.0\).

Such fits of powder magnetization data are a good but nevertheless not the best way to obtain accurate values of \(D\) and \(g\).[1] An alternative and particularly sensitive technique for getting accurate values of \(D, g\) and other spin Hamiltonian parameters is HFEPR spectroscopy, and many such studies have been carried out on Mn\textsubscript{12} complexes to date.[34]
• \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4].2\text{MeCO}_2\text{H}.4\text{H}_2\text{O}]\):

A representative plot of the magnetization (M) data for a microcrystalline powder sample of \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4].2\text{MeCO}_2\text{H}.4\text{H}_2\text{O}\) collected at various fields (H) and low temperatures (<10 K) is shown in Fig. given below, plotted as \(M/N\mu_B\) vs. \(H/T\) (N is Avogadro's constant, \(\mu_B\) is the Bohr magneton).[1] For complexes populating only the ground state and possessing no axial zfs (\(D = 0\)), the isofield lines would all superimpose and saturate at a value of \(gS\). But the data in Fig. clearly do not superimpose, which indicate a significant \(D\) value. The best fit is shown as the solid lines, and the fit parameters are \(S = 10, D = -0.50\text{ cm}^{-1}\), and \(g \sim 2.0\).

![Isofield plots of reduced magnetization \((M/N\mu_B)\) vs. \(H/T\) for microcrystalline \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4].2\text{MeCO}_2\text{H}.4\text{H}_2\text{O}\) at the indicated fields. The solid lines show the single fit using all of the data points.](image)

Fig. 4.3: Isofield plots of reduced magnetization \((M/N\mu_B)\) vs. \(H/T\) for microcrystalline \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4].2\text{MeCO}_2\text{H}.4\text{H}_2\text{O}\) at the indicated fields. The solid lines show the single fit using all of the data points.
• [Mn$_{12}$O$_{12}$(NO$_3$)$_4$(O$_2$CCH$_2$Bu')$_{12}$(H$_2$O)$_4$]:

Variable-temperature DC magnetic susceptibility ($\chi_M$) data collected in the 2.00-300 K range in a 10 kG (1 T) magnetic field is shown below. Shown in Fig.4.4, is a plot of the data as reduced magnetization (M/N$_{\mu_B}$) versus H/T. The non-superimposition of the isofield lines clearly indicates the presence of ZFS. The data can be fit assuming only the ground state is populated at these temperatures, incorporating axial ZFS (D$\hat{S}_z^2$) and Zeeman interactions, and incorporating a full powder average of the magnetization.[27] The best fit is shown as solid lines in figure, and the fitting parameters in this case are S=10, g=1.92, and D= -0.40 cm$^{-1}$ = -0.58 K. Thus, the replacement of four carboxylate groups with four NO$_3^-$ groups does not change the ground state, a result consistent with the minimal structural perturbation of the core resulting from this substitution.

Fig.4.4: Plot of reduced magnetization (M/N$_{\mu_B}$) versus H/T for [Mn$_{12}$O$_{12}$(NO$_3$)$_4$(O$_2$CCH$_2$Bu')$_{12}$(H$_2$O)$_4$.H$_2$O at 10 (▽), 20 (△), 30 (■), 40 (▲), 50 (▲), 60 (□), and 70 (●) kG. The solid lines are fits.
• [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_6$(O$_2$CET)$_8$(H$_2$O)$_3$]:

Variable-temperature dc magnetic susceptibility data[28] has been collected on the complex in the 2.00-300 K range in a 10 kG (1 T) magnetic field. Reduced magnetization (M/N$\mu_B$) versus H/T plot is shown below, where N is Avogadro's number and $\mu_B$ is the Bohr magneton. The nonsuperimposition of the isofield lines clearly indicates the presence of ZFS. The data can be fit assuming only the ground state is populated at these temperatures, using the methods[53,54] involving diagonalization of the spin Hamiltonian matrix including axial ZFS (D$S_z^2$) and Zeeman interactions and incorporating a full powder average of the magnetization. The best fits are shown as solid lines in figure, and the fitting parameters were S=10, g =1.89, and D = $-0.45\text{cm}^{-1}$ = $-0.65\text{K}$.

![Figure 4.5](image)

**Fig.4.5:** Plot of $M/N\mu_B$ vs. $H/T$ for complex [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_6$(O$_2$CET)$_8$(H$_2$O)$_3$] at the indicated applied fields.
Variable-temperature dc magnetic susceptibility data collected on complex are in the 2.00-300 K range in a 10 kG (1 T) magnetic field. Plot of the data as reduced magnetization ($M/N\mu_B$) versus $H/T$, where $N$ is Avogadro's number and $\mu_B$ is the Bohr magneton is shown below. The nonsuperimposition of the iso-field lines clearly indicates the presence of ZFS. The data are fit assuming only the ground state is populated at these temperatures, using the methods[53,54] involving diagonalization of the spin Hamiltonian matrix including axial ZFS ($D\hat{S}_z^2$) and Zeeman interactions and incorporating a full powder average of the magnetization. The best fits are shown as solid lines in figure and the fitting parameters are $S =10$, $g= 1.89$, and $D = -0.45 \text{ cm}^{-1}$, $E = -0.65 \text{ K}$. These demonstrate that the presence of two types of carboxylate ligands with distinctly different basicities does not significantly perturb the properties of the Mn$_{12}$ complexes.

![Graph](image)

**Fig.4.6:** Plot of $M/N\mu_B$ vs. $H/T$ for complex [Mn$_{12}$O$_{12}$(O$_2$CCCHCl)$_8$(O$_2$CCBH$_2$Bu')$_8$(H$_2$O)$_3$] at the indicated applied fields. The solid lines are fits of the data.[28]
DC magnetic susceptibility data collected was in the 2.00–300 K range in a 0.5 T magnetic field. A theoretical treatment of the susceptibility data via the Kambé method [55] to determine the individual pairwise Mn2 exchange interactions was not possible owing to the topological complexity and low symmetry of the Mn12 core. Instead, the ground state spin of complex [Mn12O12(O2CMe)8(O3SPh)8(H2O)4] can be determined from magnetization (M) measurements in the 1.80–4.00 K temperature range and 2.0–7.0 T field range, where N is Avogadro’s number, μB is the Bohr magneton, and H is the applied magnetic field. The obtained data are plotted as (M/NμB) vs. H/T in Fig.4-7. The non-superposition of the iso-field lines in figure is indicative of the presence of strong ZFS. The obtained fit of the data,[26,27] gives S = 10, g = 1.96 and D ~0.34 cm⁻¹ (0.49 K).[56] Thus, this complex retains the same spin as [Mn12O12(O2CMe)16(H2O)4], with fitting parameters typical for [Mn12O12(O2CR)16(H2O)4] clusters. The S = 10 value shows that, as previously discussed in the mixed-carboxylate [Mn12O12(O2CR)8(O2CR’)8(H2O)4] clusters, the presence of two types of ligands with distinctly different basicities does not affect the large ground state S value of the Mn12 complex.[27]

Fig.4.7: Plot of reduced magnetization (M/NμB) versus H/T for complex [Mn12O12-(O2CMe)8(O3SPh)8(H2O)4] in applied fields of 2 (▽), 3 (∗), 4 (Δ), 5 (▼), 6 (○) and 7(▲) Tesla. The solid lines are the fit of the data.
Magnetization data has been found in 10—70 kG and 1.80—4.00 K ranges, and are plotted as $M/N\mu_B$ vs. $H/T$ in Fig.4.8. Fitting of these data gave $S=10$, $D=-0.27$ cm$^{-1}$ = 0.39 K, $g=2.00$. The ground state spin is thus similar to $S=10$ or 19/2 values for the neutral Mn$_{12}$ and mono anionic [Mn$_{12}$] complexes, respectively. However, the anisotropy, as reflected in the absolute value of $D$, decreases as the Mn$_{12}$ complex gets progressively reduced, which is consistent with a decrease in the Mn$^{III}$ content; JT distortions of the Mn$^{III}$ ions are the main source of the molecular anisotropy. The S (D) values obtained from reduced magnetization fittings for the three oxidation levels of the family of Mn$_{12}$ dichloroacetate derivatives are: [Mn$_{12}$]$^{10}$ ($-0.45$ cm$^{-1}$); [Mn$_{12}$]$^{19/2}$ ($-0.34$ cm$^{-1}$); [Mn$_{12}$]$^{2-}$10 ($-0.27$ cm$^{-1}$). The spin value does not change on two-electron reduction and that the two-electron reduced Mn$_{12}$ complex (PPh$_4$)$_2$[Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_{16}$(H$_2$O)$_4$] functions also as an SMM.[57]
Variable-temperature DC magnetic susceptibility data has been collected in the 2.00-300 K range in a 10 kG magnetic field. A plot of the reduced magnetization ($M/N\mu_B$) versus $H/T$ is given in Fig. The data were fit by diagonalization of the spin Hamiltonian matrix incorporating axial ZFS ($D S_z^2$) and Zeeman interactions and assuming only the ground state to be populated at these temperatures. The best fit is shown as solid lines and the fitting parameters were $S=10$, $g=1.83$, and $D= -0.42$ cm$^{-1} = 0.60$ K. Complex [Mn$_{12}$O$_{12}$(O$_2$CPh)$_7$(O$_2$PPh$_2$)$_9$(H$_2$O)$_4$] was also reported to have an $S=10$ ground state, with $D= -0.50$ cm$^{-1} = -0.72$ K. Thus, the replacement of nine benzoate groups with nine Ph$_2$PO$_2$ groups does not change the ground state, a result consistent with the minimal structural perturbation of the core resulting from the ligand replacement.

![Fig.4.9: Plot of $M/N\mu_B$ versus $H/T$ for complex [Mn$_{12}$O$_{12}$(O$_2$CPh)$_7$(O$_2$PPh$_2$)$_9$(H$_2$O)$_4$]. 3CH$_2$Cl$_2$ at different fields.](image)
Solid-state dc magnetization measurements were in the range 1.8–300 K in a field of 10.0 kG. The data were fit using a full-matrix diagonalization approach; the best fits were with $S = 6$, $g = 2.09$, $D = 20.8$ cm$^{-1}$ and $S = 7$, $g = 1.79$, $D \approx 20.6$ cm$^{-1}$, which were of comparable quality but poorer than those normally obtained. This is a common problem in higher nuclearity Mn$_x$ systems[59] and is assignable to relatively low-lying excited states, particularly when Mn$^{11}$ ions are present since these typically give weak exchange interactions. We conclude that the molecule has $S = 6$ or 7, although we favour the latter given that $g < 2$.

![Plot of M/N$\mu_B$ vs H/T for [Mn$_{12}$O$_8$Cl$_4$(O$_2$CPh)$_8$(hmp)$_6$] in eicosane at 20 (●), 30 (▲), 40 (▼), and 50 (●) kG.](image)
• [Mn$_{12}$O$_{12}$(C$_4$H$_5$O$_2$)$_{16}$(H$_2$O)$_4$].H$_2$O:

The $M/N\mu_B$ versus $H/T$ plots at different fields do not superimpose which indicate that the ground state of these complexes is zero-field split. The data is least-squares fit. The best fit for this complex is $S \sim 10$, $D \sim -0.44$ cm$^{-1}$, and $g \sim 2.01$.

![Graph showing $M/N\mu_B$ versus $H/T$](image)

Fig.4.10: Plot of the reduced magnetization, $M/N\mu_B$ versus $H/T$ for complex at 2.0–4.0 K range for the magnetic fields of (●) 50, (○) 40, (■) 30 and (□) 20 kG.

• [Mn$_{12}$O$_8$Cl$_4$(O$_2$CPh)$_6$(hep)$_6$]:

Solid-state dc magnetization measurements were performed on [Mn$_{12}$O$_8$Cl$_4$(O$_2$CPh)$_6$(hep)$_6$] in the range 1.8–300 K in a 10.0 kG field. The ac and dc data are essentially superimposable (not shown) except at the lowest temperatures and appear to be heading for $\chi_M T = 0$ cm$^3$ mol$^{-1}$ K at 0 K, suggesting an $S = 0$ ground state. Its very different $S$ value compared with [Mn$_{12}$O$_8$Cl$_4$(O$_2$CPh)$_6$(hmp)$_6$] is due to the core isomerism, which affect many of the Mn2 pairwise exchange interactions in the core.

No $\chi_M$” signal is observed for this complex and thus it is not a SMM.
AC magnetic susceptibility studies:

A diagnostic technique for observing slow magnetization relaxation of a SMM is ac magnetic susceptibility.[44] In an AC susceptibility experiment, a weak field (typically 0.1–0.5 mT) oscillating at a particular frequency (ν) is applied to a sample to probe the dynamics of the magnetization (magnetic moment) relaxation. A species that possesses a magnetization relaxation mechanism that is slower than the oscillating field produced by the magnetometer cannot stay in phase with this field, and will exhibit a peak in the out-of-phase component of the ac susceptibility and there will be a corresponding decrease in the in-phase signal. This peak (out of phase) corresponds to a rate in which the magnetic moment of the SMM ‘flips’ close to the rate of the operating frequency of the instrument. On the other hand, a simple paramagnet will not produce a peak in the out-of-phase component of the ac susceptibility, since the rate of the ‘flipping’ of the magnetic moment of such a species (∼109 Hz) occurs well above the typical (1–1500 Hz) operating frequencies of an ac magnetometer.

The origin of the out-of-phase peak observed for the first discovered SMM has been the focus of considerable research.[7] One frequency-dependent peak is observed for the Mn12-acetate in the 4–7 K region. A puzzling observation[8] for several Mn12 type molecules is that they may display two, instead of one, frequency dependent peaks in the out-of-phase ac susceptibility response. These peaks often occur in the 2–3 K (low temperature) and 4–7 K (high temperature) ranges.[60] At low enough temperature, where the thermal energy is lower than the barrier for relaxation, kT<|D| m2, the magnetization of the molecule cannot relax fast enough to keep in-phase with the oscillating field and the rate at which the magnetic moment of a molecule flips becomes sluggish and this relaxation phenomenon appears as an out-of-phase ac susceptibility peak within a certain range of frequencies. This leads to one out-of-phase ac signal per Mn12 molecule or for a collection of identical Mn12 molecules. However, it does not explain why a given complex would exhibit two out-of-phase ac signals. Therefore, the molecule will exhibit a frequency-dependent out of phase signal indicative of slow magnetization relaxation. Frequency-dependent out of phase signals are an important indicator of SMMs.
Thus, if a collection of SMM’s is maintained at a certain temperature and the frequency of the AC magnetic field is varied, a maximum in the out of phase (\(\gamma_M\)) signal will occur when the oscillation frequency of the field equals the rate at which a molecule can interconvert between the halves of the potential energy double well shown below:

![Double-well potential energy plot](image)

Fig. 4.11: Double-well potential energy plot for an \(S = 10\) molecule with axial symmetry and easy-axis type anisotropy. The energy separation between the \(M_s = \pm 10\) and \(M_s = 0\) orientations of the magnetization is given by \(S^2 |D|\).

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,

\[
\frac{1}{\tau} = \left(\frac{1}{\tau_0}\right) \exp(-U_{eff}/kT)
\]

Or

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

Where \(1/\tau = \) relaxation rate,
\(1/\tau_0 = \) pre-exponential term,
\(U_{eff} = \) effective energy barrier,
\(kT = \) thermal energy,
\(k = \) Boltzmann constant
- \([\text{Mn}_{12}\text{O}_{12}\text{(O}_2\text{CMe})_{16}\text{(H}_2\text{O})_4\text{]}\cdot2\text{MeCO}_2\text{H}\cdot4\text{H}_2\text{O}]:\)

The representative \(\chi_M T\) plot for this SMM is shown below. The observed value of \(\chi_M T\) at room temperature, is 19.4 emu mol\(^{-1}\)K which is much less than expected (31.5 emu mol\(^{-1}\)K) for uncoupled spins. This value indicates antiferromagnetic coupling. The maximum value of \(\chi_M T\) at room temperature is 55.6 emu mol\(^{-1}\)K.

![\chi_M T versus T graph for Mn\(_{12}\)-Acetate.](image)

**Fig.4.12:** \(\chi_M T\) versus T graph for Mn\(_{12}\)-Acetate.

**Fig.4.13:** \(\chi''\) versus T graph for Mn\(_{12}\)-Acetate.

Next proof of SMM is associated with temperature independence of relaxation time. For Mn\(_{12}\)ac, below 2K relaxation time becomes experimentally long.[7,19]

![Plot of log\(\tau\) versus Temperature of Mn\(_{12}\)-acetate.](image)

**Fig.4.14:** Plot of log\(\tau\) versus Temperature of Mn\(_{12}\)-acetate.
• [Mn₁₂O₁₂(O₂CCH₂Br)₁₆(H₂O)₄]:

The representative $\chi_M'$ (as $\chi_M'T$) and $\chi_M''$ data for vacuum dried [Mn₁₂O₁₂(O₂CCH₂Br)₁₆(H₂O)₄] are shown in Fig.4.14. The value of $\chi_M'T$ is $\sim$50 cm$^3$ K mol$^{-1}$ above $\sim$9 K, which is consistent with $S = 10$ and $g$ slightly less than 2.0, in agreement with dc fit data for this compound.[33] At lower temperatures, there is a frequency-dependent decrease in the $\chi_M'T$ and concomitant frequency-dependent increase in the $\chi_M''$ signals. At still lower temperatures of $\sim$2.5 K, there is a second feature in both $\chi_M'T$ and $\chi_M''$, indicating the presence of a small fraction of faster-relaxing Mn₁₂ species in the sample. This is characteristic of a JT isomer involving an abnormally oriented Mn$^{III}$ JT axis (vide supra), which has a smaller barrier to magnetization relaxation and thus is a faster-relaxing, so-called “lower-temperature” (LT) form. Comparison of these $\chi_M'T$ and $\chi_M''$ plots for vacuum-dried samples with those for wet (with mother liquor) samples shows that although dried samples exhibit both LT and “higher temperature” (HT) signals, the wet samples show only the HT signal.[33] This indicates that the LT signal arises from the loss of solvent molecules and its resulting effect on the crystal lattice and Mn₁₂ environments.

![Fig.4.15: In-phase $\chi_M'$ (as $\chi_M’T$) and out-of-phase $\chi_M''$ signals for a microcrystalline sample of [Mn₁₂O₁₂(O₂CCH₂Br)₁₆(H₂O)₄.](image)
- \([\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^\text{t})_{12}\text{H}_2\text{O}_4])\):

The AC susceptibility of this complex is shown in fig.4.12. The upper panel shows the \(\chi_M^\prime\)T versus T plot, where \(\chi_M^\prime\) is the in-phase magnetic susceptibility, and the lower panel shows the \(\chi_M^\prime\prime\) versus T plot. The frequency-dependent decrease in the \(\chi_M^\prime\)T versus T plot is a signature of the magnetization relaxation rate becoming comparable with the AC frequency. If so, a \(\chi_M^\prime\prime\) signal should appear at the corresponding temperatures, and the \(\chi_M^\prime\prime\) versus T plot shows that this is indeed the case; there are frequency-dependent \(\chi_M^\prime\prime\) signals in the 4-7 K range, which demonstrates that complex is an SMM. Only one \(\chi_M^\prime\prime\) peak is seen at each frequency, and thus the sample does not contain the new phenomenon of Jahn-Teller isomerism identified recently, whereby some Mn\(_{12}\) molecules possess an orientation of one JT axis that is equatorial rather than axial and which causes an increase in the relaxation rate and a corresponding \(\chi_M^\prime\prime\) peak in the 2-4 K region.[35] Moreover, the \(\chi_M^\prime\)T value at its near plateau value in the 10 K region can be used to determine the ground state of complex, assuming that only the ground state is significantly populated at these temperatures. The \(\chi_M^\prime\)T value of \(-52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}\) corresponds to an S =10 system with \(g =1.94\), consistent with the reduced magnetization results.

Fig.4.16: In-phase (\(\chi_M^\prime\)) and out-of-phase (\(\chi_M^\prime\prime\)) AC susceptibility signals for \([\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^\text{t})_{12}\text{H}_2\text{O}_4])\text{H}_2\text{O}\) at 100 (\(\bullet\)), 10 (\(\bigtriangledown\)), 50 (\(\Delta\)), 1000 (\(\square\)) and 1500 (\(\bullet\)) Hz.
Arrhenius equation is also followed by this SMM and the observed values are: $U_{eff} = 50.0 \text{ cm}^{-1} = 72.0 \text{ K}$ and $1/\tau_0 = 1.9 \times 10^8 \text{ s}^{-1}$ which are similar to that for other Mn$_{12}$ SMMs.

![Graph](image)

Fig.4.17: Plot of the natural logarithm of relaxation rate, $\ln(1/\tau)$ versus inverse temperature for $[\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^t)_4(\text{H}_2\text{O})_8].\text{H}_2\text{O}$.

- $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCHCl}_2)_8(\text{O}_2\text{CR})_8(\text{H}_2\text{O})_3] (R = \text{CH}_2\text{Bu}^t, \text{Et})$:

The ac susceptibilities of both the complexes in a 3.5 G ac field oscillating at various frequencies in the range indicated are shown below.[17]

![Graph](image)

Fig.4.18: In-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) ac susceptibility signals for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCHCl}_2)_8(\text{O}_2\text{CR})_8(\text{H}_2\text{O})_3] (R = \text{CH}_2\text{Bu}^t)$ at the indicated frequencies.

73
**Fig.4.19:** In-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) ac susceptibility signals for [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_8$(O$_2$CCEt)$_8$(H$_2$O)$_3$] at the indicated frequencies.

The figures show the frequency-dependent decrease in the $\chi_M''$T versus T plots which is a signature of the magnetization relaxation rate. Appearance of $\chi_M''$ signals in the 4-7 K range confirms that both the complexes display the super-paramagnetic-like properties of SMMs. Only one $\chi_M''$ peak is seen at each frequency, and these samples therefore do not exhibit the new phenomenon of Jahn-Teller isomerism,[51] whereby some Mn$_{12}$ molecules possess an abnormal orientation of one JT axis. The latter leads to faster relaxation rates and $\chi_M''$ peaks at correspondingly lower temperatures (2-4 K). Also the $\chi_M'T$ value at its near plateau value at ~10 K of 50-52 cm$^3$ K mol$^{-1}$ for both can be used to determine the ground state S values of the complexes, assuming only the ground state is occupied at this temperature. A $\chi_M'T$ value of ~51 cm$^3$K mol$^{-1}$ corresponds to an S =10 system with g =1.93.

Magnetization follows the Arrhenius equation and the data obtained for [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_8$(O$_2$CCH$_2$Bu')$_8$(H$_2$O)$_3$] is $U_{\text{eff}}$ =50 cm$^{-1}$ = 72 K and 1/$\tau_0$ = 1.3×10$^8$ s$^{-1}$ and for [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_8$(O$_2$CCEt)$_8$(H$_2$O)$_3$], $U_{\text{eff}}$ = 49 cm$^{-1}$ = 71 K and 1/$\tau_0$ = 1.6×10$^8$ s$^{-1}$. 
Fig. 4.20: Plots of the natural logarithm of relaxation rate, ln(1/τ), vs inverse temperature for [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_6$(O$_2$CR)$_6$(H$_2$O)$_3$] (R= CH$_2$Bu', Et) respectively.

- [Mn$_{12}$O$_{12}$(O$_2$CMe)$_8$(O$_3$SPh)$_8$(H$_2$O)$_4$]:

Ac susceptibility studies performed on this complex are in the 1.80–10.0 K range in a 0.35 mT field oscillating at frequencies (ν) up to 1000 Hz. The in-phase (χ'_M) and out-of-phase (χ''_M) signal are plotted vs. T in Fig. 3. The figure clearly shows frequency-dependent decrease in χ'_M T at T < 10 K, concomitant with the appearance of a frequency-dependent out-of-phase (χ''_M) signal. These indicate that the magnetization of this complex cannot relax fast enough to stay in-phase with the oscillating field, and this is a strong indication that this complex is a single molecule magnet (SMM). At each frequency, there is only one χ''_M peak, and complex does not therefore exhibit JT isomerism. The latter is the presence of an abnormally oriented JT axis, equatorial with respect to the Mn$_{12}$ disk, that leads to a lower barrier to magnetization relaxation and a χ''_M peak at consequently lower temperatures.[62] Complex is thus present as exclusively the normal, slower-relaxing JT isomer.
Fig. 4.21: Plot of the in-phase (as $\chi_M' T$) and out-of-phase (as $\chi_M''$) ac susceptibility signals vs. temperature for complex $[\text{Mn}_{12} \text{O}_{12}(\text{O}_2\text{CMe})_8(\text{O}_3\text{SPh})_8(\text{H}_2\text{O})_4]$ at the indicated oscillation frequencies.

An effective energy barrier ($U_{\text{eff}}$) of 67 K and a pre-exponential factor ($\tau_0$) of $6.6 \times 10^9$ s has been found for this SMM. The $U_{\text{eff}}$ value falls within the normal range 42–50 cm$^{-1}$ (60–72 K) which has been observed for several $[\text{Mn}_{12} \text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ complexes.

Fig. 4.22: Arrhenius plot for $[\text{Mn}_{12} \text{O}_{12}(\text{O}_2\text{CMe})_8(\text{O}_3\text{SPh})_8(\text{H}_2\text{O})_4]$ using ac $\chi_M''$ data ($\Delta$) and dc magnetization decay data ($\bullet$).
- [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu')$_{16}$(Bu$'$OH)(H$_2$O)$_3$]:

The in-phase ($\chi_M''^T$) and out-of-phase ($\chi_M''$) AC susceptibility signals for this complex are shown below. Extrapolation of the in-phase data to 0 K from above $\sim 9$ K gives $\chi_M''^T \sim 56$ cm$^3$Kmol$^{-1}$, which indicates an $S = 10$ ground state with $g \sim 2.0$, which is the expected ground state spin of a Mn$_{12}$ complex. At lower temperatures, there is a frequency-dependent decrease in $\chi_M''^T$ and a concomitant increase in $\chi_M''$, which is an important indicator to be an SMM.

Fig.4.23: Plot of the in-phase ($\chi_M''^T$) and out-of-phase ($\chi_M''$) AC susceptibility signals versus temperature for [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu')$_{16}$(Bu$'$OH)(H$_2$O)$_3$].
The value of the effective kinetic energy barrier (\(U_{\text{eff}}\)) to magnetization relaxation determined is \(U_{\text{eff}} = 62.6\text{K}\) and \(\tau_0 = 9.1 \times 10^{-9}\text{s}\) \((1/\tau_0 = 1.1 \times 10^8\text{s}^{-1})\).

![Graph: Plot of the natural logarithm of the magnetization relaxation rate versus 1/T for \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^\dagger)_{10}(\text{Bu}^\dagger\text{OH})(\text{H}_2\text{O})_3].\)](image)

**Fig.4.24:** Plot of the natural logarithm of the magnetization relaxation rate versus 1/T for \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^\dagger)_{10}(\text{Bu}^\dagger\text{OH})(\text{H}_2\text{O})_3].\)

- **[Mn\(_{12}\)O\(_{12}(\text{C}_4\text{H}_5\text{O}_2)_{10}(\text{H}_2\text{O})_4].\text{H}_2\text{O}**: The plot of \(\chi T\) versus T for this complex is shown in the figure given below. At 320 K, the value of \(\chi T\) for this complex (21.7 cm\(^3\) K mol\(^{-1}\)) is very close to the spin-only value of 19.0 cm\(^3\) K mol\(^{-1}\) expected for a cluster comprising 8Mn\(^{III}\) and 4Mn\(^{IV}\) non interacting centers. From 320 to 120 K, the plot show a gradual decrease and then \(\chi T\) increases rapidly until it reaches a maximum at 15 K with \(\chi T\) value of 55.4 cm\(^3\) K mol\(^{-1}\). This value is again close to the spin-only value expected for an S ~ 10 (55cm\(^3\) Kmol\(^{-1}\)) ground state with \(g \sim 2.0\). Complex exhibit frequency-dependent out-of-phase ac signal in the range of 4–7 K. The plot of the out-of-phase susceptibility \(\chi_M^*\) signal versus temperature is also shown in the figure.
Fig. 4.25: Plot of $\chi_T$ versus $T$ for complex $[{\text{Mn}}_{12}\text{O}_{12}(\text{C}_4\text{H}_9\text{O}_2)_{16}(\text{H}_2\text{O})_4].\text{H}_2\text{O}$ (left) and $\chi''_M$ versus $T$ for complex oscillating at 50 Hz ($\Delta$), 250 Hz ($\bullet$) or 1000 Hz ($\blacksquare$) (right).

The least-square fit of the ac susceptibility relaxation data gives energy barrier of 65.4 K and attempt frequencies $t_0 \sim 2.43 \times 10^{-9}$ s.

• $[{\text{Mn}}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{C}_5\text{H}_11\text{OH})_4]$: 

The corresponding in-phase ($\chi_M^I$) and out-of-phase ($\chi''_M$) AC susceptibility signals for this complex are shown in figure. Extrapolation of the in-phase data to 0 K from above 9 K again gives $\sim 55$ cm$^3$Kmol$^{-1}$ which indicates an $S = 10$ ground state with $g \sim 2.0$. Magnetization relaxation rate for this SMM is slower than $[{\text{Mn}}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{Bu}^t\text{OH})(\text{H}_2\text{O})_3]$. 

Fig. 4.26: Plot of the natural logarithm of the magnetization relaxation rate versus $1/T$ for $[{\text{Mn}}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{Bu}^t\text{OH})\text{H}_2\text{O})_3]$. 

79
Fig. 4.26: Plot of the in-phase ($\chi_M'$) and out-of-phase ($\chi_M''$) AC susceptibility signals versus temperature for [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$'$)$_{16}$(C$_5$H$_{11}$OH)$_4$].

Arrhenius equation followed by this SMM gives the values: $U_{eff}$=71.2K and $\tau_0=1.1 \times 10^{-8}$ s ($1/\tau_0 =9.1 \times 10^7$ s$^{-1}$). Data clearly indicates that [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$'$)$_{16}$(C$_5$H$_{11}$OH)$_4$] has the smaller $1/\tau_0$ by about 17% and the higher $U_{eff}$ by about 14% than that for [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$'$)$_{16}$(Bu$'$OH)(H$_2$O)$_3$]. These differences in $1/\tau_0$ and $U_{eff}$ both serve to yield a slower relaxation rate for former versus latter at a given temperature.

Fig. 4.27: Plot of the natural logarithm of the magnetization relaxation rate versus $1/T$ for [Mn$_{12}$O$_{12}$(O$_2$CCH$_2$Bu$'$)$_{16}$(C$_5$H$_{11}$OH)$_4$].
• \([\text{Mn}_{12}O_{12}(O_2CPh)_7(O_2PPPh_2)_3(H_2O)_4]\cdot 3\text{CH}_2\text{Cl}_2\):

Plots of the in-phase component (\(\chi_M\)) and the out-of-phase component (\(\chi_M''\)) versus \(T\) at different frequencies are shown in fig. 4.28. The \(\chi_M T\) signal shows a frequency dependent decrease at \(T<5 \text{ K}\) which indicates slow relaxation. The \(\chi_M T\) value remains constant at a value of 49 cm\(^3\)Kmol\(^{-1}\) between 10 and 3-4K. Below this, the value of \(\chi_M T\) decreases rapidly. Simultaneously with the sharp decrease in \(\chi_M T\), the appearance of an out-of-phase signal (\(\chi_M''\)) is observed. A frequency-dependent drop in the in-phase component and an appearance of an out-of-phase component of the AC magnetic susceptibility are indicators of a SMM.

**Fig. 4.28:** Plot of the AC magnetic susceptibility data for \([\text{Mn}_{12}O_{12}(O_2CPh)_7(O_2PPPh_2)_3(H_2O)_4]\cdot 3\text{CH}_2\text{Cl}_2\) showing the in-phase (\(\chi_M\)) (top) and out-of-phase (\(\chi_M''\)) (bottom) signals versus temperature.

Arrhenius equation followed by this SMM gives the values of \(t_0 = 5.9 \times 10^9 \text{ s}\) and \(U_{eff} = 28 \text{ cm}^{-1}\) which is very smaller as compared to that of other \(\text{Mn}_{12}\) SMMs and is consistent with molecules possessing abnormal JT axes (‘faster relaxing’) \(\text{Mn}_{12}\) complexes.
Fig. 4.29: Plot of $\ln(1/\tau)$ versus inverse temperature for complex $[\text{Mn}_{12} \text{O}_{12} (\text{O}_2\text{CPh})_7 (\text{O}_2\text{PPh}_2)_6 (\text{H}_2\text{O})_4] \cdot 3\text{CH}_2\text{Cl}_2$.

- $[\text{Mn}_{12} \text{O}_{12} (\text{O}_2\text{CCHCl}_2)_16 (\text{H}_2\text{O})_4]^{2+} (z=0-3)$:

$[\text{Mn}_{12}]^{2+} (z=0-3)$ family exhibit the out-of-phase $\chi''$ signals indicative of the slow relaxation of SMMs. Figure 4.30 shows the comparison of the $\chi''$ signals for $[\text{Mn}_{12} \text{O}_{12} (\text{O}_2\text{CCHCl}_2)_16 (\text{H}_2\text{O})_4]^{2+}$ at two ac frequencies. [63] The peak moves progressively to lower temperature with increasing extent of reduction with decreasing relaxation barrier.

Fig. 4.30: Comparison of the $\chi''$ vs. $T$ plots for $[\text{Mn}_{12} \text{O}_{12} (\text{O}_2\text{CCHCl}_2)_16 (\text{H}_2\text{O})_4]^{2+} (z = 0-3)$ at 1000 Hz (top) and 50 Hz (bottom).
Arrhenius plot for \([\text{Mn}_{12}]^{z}\) \((z=0,1,2)\) shows that decrease in \(U_{\text{eff}}\) value on progressive reduction reveal the faster magnetization reversal and the decreasing Mn\textsuperscript{III} content on reduction.

![Arrhenius plot for \([\text{Mn}_{12}]^{z}\) \((z=0,1,2)\) showing decrease in \(U_{\text{eff}}\) value on progressive reduction.](image)

**Fig. 4.31:** Plot of the natural logarithm of relaxation rate, \(\ln(1/\tau)\), vs. inverse temperature for \([\text{Mn}_{12}]^{z}\) \((z=0,1,2)\)

The magnetic properties of Mn\textsubscript{12} and other SMMs are very sensitive to their environment. The presence of solvent molecules and their positional or orientational variation or disorder results to a significant distribution of molecular environments, contributing to a resulting distribution of \(D\) values and relaxation barriers \(U_{\text{eff}}\). QTM step broadening in the hysteresis loops and others. It can even lead to completely different magnetic behaviours.\(^{[1]}\)

- \([\text{Mn}_{12} \text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_16(\text{H}_2\text{O})_4].\text{CH}_2\text{Cl}_2.\text{MeNO}_2\)
- \([\text{Mn}_{12} \text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_16(\text{H}_2\text{O})_4].\text{CH}_2\text{Cl}_2.\text{MeCN}\):

This is the case even though they have almost identical unit cells and are essentially superimposable except that the latter has an MeCN molecule at the position of the MeNO\textsubscript{2} in the former. Their ac \(\chi''\) versus \(T\) plots are shown in figure and show that the isomer with the abnormal JT orientation is the LT (i.e. faster relaxing) form.
Accordingly, Arrhenius plots give $U_{\text{eff}}$ values of 62 and 42 K for the HT and LT isomers, respectively. Possible origins of the faster relaxation in the LT isomer are:

(i) Lower symmetry core and the faster tunnelling

(ii) Different QTM rates

(iii) Very lowlying excited state S manifold nesting with the ground state and providing lower-energy relaxation pathways.

Fig. 4.32: $\chi''$ versus $T$ plots for $[\text{Mn}_{12}O_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_6(\text{H}_2\text{O})_4].\text{CH}_2\text{Cl}_2.\text{MeNO}_2$ (LT) (top) and $[\text{Mn}_{12}O_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_6(\text{H}_2\text{O})_4].\text{CH}_2\text{Cl}_2.\text{MeCN}$ (HT) (bottom).
Magnetic Hysteresis and Magnetic Quantum Tunneling:

The significant $\text{Mn}_{12}$ relaxation barriers lead to a ‘freezing’ of the magnetization reversal below a sufficiently low temperature, the ‘blocking temperature’ ($T_B$), which is typically in the 3–4 K regions for $\text{Mn}_{12}$ complexes. As a result, hysteresis loops are seen in magnetization vs. applied dc field scans. These are best investigated on single-crystal samples using a micro-SQUID apparatus.

Magnetization hysteresis is the diagnostic behavior of a magnet, and is thus the ultimate proof that a molecule is an SMM. The hysteresis loops of SMMs differ markedly from those of bulk traditional (i.e. 3-D) magnetic materials in exhibiting an increasing co-ercivity (half the loop width at $M/M_s = 0$) with decreasing temperature and with increasing field sweep rate. Moreover, the loops for SMMs are not smooth but display steps due to QTM at periodic field values. The steps are at field positions where $M_s$ levels of the $S = 10$ manifold on one side of the double-well energy barrier are degenerate with $M_s$ levels on the other side (Fig. 8), and QTM can thus occur. QTM causes an increase in the magnetization relaxation rate, giving the vertical jump (step) in the loop.

![Energy and Spin Projection Diagrams](image-url)

**Fig.4.33:** Plot (top) showing $M_s$ states of the spin vector of a $\text{Mn}_{12}$ SMM using $S = 10$ and negative $D$ and (bottom)the barrier ($U$) to relaxation as being the energy difference between the $M_s=0$ and 10 states.

85
The step size decreases with increasing field scan rate, as predicted from the standard Landau–Zener model for tunnelling between two states.[61] Although QTM is a characteristic property of all SMMs, and steps are essentially always seen in the hysteresis loops for the Mn$_{12}$ family. This is not always seen for other SMMs. In many cases, the steps are often broadened, mainly for larger nuclearity SMMs. The broadening is because of significant distribution of molecular environments which give a correspondingly significant distribution of step positions, or to a high density of low-lying excited states. QTM can occur when a -$M_s$ state on one side of a symmetric or asymmetric potential energy double well is equienergetic with a $+M_s + n$ state ($n = \text{integer}$) on the other side. As a result, the magnetization can reverse from “spin up” to “spin down” by tunneling through the anisotropy barrier rather than going over it.

The first step is expected when the applied field is returned to zero after it has saturated the magnetization in a given direction (“spin up”). In zero fields, the potential energy double well is symmetric, and all -$M_s$ states are degenerate with the corresponding $+M_s$ states, and QTM can occur. When the applied field is reversed, further steps at approximately regular intervals appear when -$M_s$ states are degenerate with $+M_s + n$ states in an asymmetric double well. The steps are regularly spaced in applied field and invariant with temperature. The field separation ($\Delta H$) is related to $D$ by the following eq.:

$$\Delta H = \left| D \right|/g\mu_B$$

The largest SMM to display QTM steps is a Mn$_{22}$ complex,[52] although many at smaller nuclearities do not. In such cases, the presence of QTM can be established by other methods, such as a temperature-independent region at very low temperatures in the Arrhenius plot.
[Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄].2MeCO₂H·4H₂O:

The cluster of Mn₁₂-Acetate shows a clear hysteresis loop as shown in fig.4.34. There are unusual stairs below the blocking temperature. The steps occur at well defined fields $H_n = n0.4 T$ where, $n=0, 1, 2, ...$. This provides the evidence for quantum tunneling because at the given field, there are pair of energy levels with the same energy. [64] In the flat portion of the loops, the relaxation time is much larger than the measuring time scale($t_m$) and in the steep portion of the loop, magnetization relaxes rapidly i.e. $t_m \approx \tau$. This hysteresis is substantially different from that of an ordered magnetic material. Unlike the hysteresis in ferromagnetic materials where the effect of applied fields is responsible for the movement of the domain walls, the hysteresis curve here arises due to acceleration of relaxation by the field. The reversibility field decreases with increasing temperature[18].

![Hysteresis loop for Mn₁₂-Acetate.](image)

Fig.4.34: Hysteresis loop of magnetization for Mn₁₂-Acetate.
• \([\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^\dagger)_12(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}]:\)

Since this SMM has a sufficiently large barrier to magnetization reversal which results in wider hysteresis loop. Inspection of the magnetization hysteresis loops shows step features at regular intervals of applied field. The steps are regularly spaced in applied field and the field separation \((\Delta H)\) for this SMM is 0.449 T which gives the value for \(|D|/g = 0.21\text{ cm}^{-1}\).

![Graph of hysteresis loop](image)

Fig.4.35: Hysteresis loop for \([\text{Mn}_{12}\text{O}_{12}(\text{NO}_3)_4(\text{O}_2\text{CCH}_2\text{Bu}^\dagger)_12(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}.\)
- \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_8(\text{O}_3\text{SPh})_8(\text{H}_2\text{O})_4]^-\):

Since this complex is a SMM, it should exhibit phenomenon of hysteresis below its blocking temperature, \(T_B\). Hysteresis loops for this SMM are shown in the figure given below. The loops are not completely smooth, instead showing the step-like features characteristic of quantum tunneling of the magnetization (QTM) through the anisotropy barrier. However, these steps are much less well defined than usual for \(\text{Mn}_{12}\) complexes. Instead, they are rather broad and poorly resolved, although clearly present at field positions of zero, \(\sim 0.65\) and \(\sim 1.3\) T.

![Diagram of hysteresis loops](image)

**Fig. 4.36:** Magnetization (M) versus magnetic field hysteresis loops for \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_8(\text{O}_3\text{SPh})_8(\text{H}_2\text{O})_4]^-\).
• $[\text{Mn}_{12} \text{O}_{12}(\text{C}_4\text{H}_5\text{O}_2)_{16}(\text{H}_2\text{O})_4].\text{H}_2\text{O}$:

The magnetic hysteresis loops of the complex are shown in Fig.4.37. The steps can also be observed for this complex like other SMMs. If all the molecules changed their direction of magnetization by thermal activation over the barrier, then the hysteresis loop would be a smooth function with no steps. The steps are due to resonance quantum mechanical tunnelling of the magnetization direction.

Fig.4.37: Plots of magnetization versus external magnetic field for complex at three temperatures in the 1.80–2.20 K range.

Lastly, hysteresis loops have also been obtained for $[\text{Mn}_{12}]^{1+}$ and $[\text{Mn}_{12}]^{2-}$ complexes, confirming them also to be SMMs. Shown in Fig. 4.38 are the loops exhibited by a single crystal of the $[\text{Mn}_{12}]^{2-}$ salt $(\text{NMe}_4)_2[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{F}_3)_{16}(\text{H}_2\text{O})_4].6\text{C}_7\text{H}_8$. Hysteresis is only observed at $\sim 1.5$ K and below, in contrast to the higher temperatures for the neutral Mn$_{12}$ complex with the same carboxylate in Fig.4.39 and consistent with a significantly smaller relaxation barrier on reduction.
Fig. 4.38: Magnetization (M) hysteresis loops for a single crystal of the $[\text{Mn}_{12}]^2^-$ salt $(\text{NMe}_4)_2[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{C}_6\text{F}_3)_{16}(\text{H}_2\text{O})_4].6\text{C}_7\text{H}_8$.

Fig. 4.39: Magnetization (M) hysteresis loops for a single crystal of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{C}-\text{C}_6\text{F}_3)_{16}(\text{H}_2\text{O})_4].3\text{CH}_2\text{Cl}_2$ showing the temperature dependence at a fixed sweep rate (top), and the sweep rate dependence at a fixed temperature (bottom).
Again, QTM steps are clearly observable at periodic values of applied field. Single crystals of $[\text{Mn}_{12}]^{3-}$ are not available for similar studies, but if they were there seems little doubt from its other properties that this oxidation state would also exhibit hysteresis loops.[1] Inspection of the steps in Fig. 15 and 16, for example, shows that those for the $[\text{Mn}_{12}]^{2-}$ complex are significantly closer together than those for the Mn$_{12}$ complex, i.e. the former has a smaller $|D|$ value than the latter.
Conclusion

We have shown in this chapter the synthesis, structure and magnetic properties of manganese clusters that have been developed up till now. This review has proven an invaluable source of collective data on this fascinating and interesting phenomenon. SMMs are interesting materials retaining all the advantages of molecular chemistry. Various methods are now available for the preparation and the controlled modification of Mn₄₈ molecules. These methods provide an array of various SMMs for all type of studies. Except Mn₂₃ family, for no other SMM type has such a large degree of controlled modification been accomplished.

The use of Mn₂₃ devices in molecular magnets to bind them has led to a great deal of interest. The controlled modification of these molecules offers many interesting studies of the Mn₂₃ family in the physics and related literature. Nevertheless, there are probably more Mn₂₃ papers in the physics than the chemistry literatures, owing to the many studies of what are mesoscale magnetic particles that have become possible from the availability of crystalline, monodisperse, often identically-oriented assemblies of SMMs.

Single molecule magnets have opened possibility for the study of physical phenomena at the edge between the microscopic quantum world and the macroscopic classical regime. Experimentally, SMMs provide a signature of quantum mechanical behavior which is derived from a combination of large spin (S) and easy axis anisotropy. SMMs also have the application feature such as in quantum computation. The effort has been in developing the SMMs with higher blocking temperature for the practical use in the upcoming generation quantum computers and magnetic data storage. Various experimental techniques have been successfully used for the study of these systems; yet, there is still requirement of neat theory to describe them.

CONCLUSION