

CHAPTER 1

Aromaticity and magnetism in metal based systems

Abstract

This chapter provides a brief account of the history and significant advances in the fields of aromaticity and magnetism. In this chapter a concise history of the origin and advancement of research in aromaticity is given which correlates the chronological development of the subjects with the evolution of new materials. The current status of the research in aromaticity, with special emphasis on the metal based aromatic molecules, is provided. Magnetism is also discussed according to the chronology of the advancement of the theory and explored materials. The effect of dimension in the magnetic properties is also discussed here. The emergence of new molecules for nanomagnets and the role of the theoretical advancement in designing such materials also discussed in this chapter.

1.1 Aromaticity

The concept of aromaticity is of central importance to the theory and practice of teaching and research in chemistry. The chemical term “aromatic” is first known to be used by August Wilhelm Hofmann in 1855.¹ Hofmann referred to a group of acids related to Benzoic acid as “aromatic acids” in his paper. In early 1860 “fatty” and “aromatic” compounds were differentiated by Kekulé.² The word aromatic was first chosen by Kekulé to refer benzene derivatives richer in carbon (kohlenstoffreichere). A precise definition of aromaticity was never given by Kekulé other than some partial definitions in the 1865/66 papers.³ In 1872, Kekulé described benzene as “a regular arrangement of the six carbon atoms”, thus implying a D_{6h} symmetric structure. However, initially benzene was drawn with alternating single and double bonds indicating a D_{3h} symmetric structure.⁴ The axiom, that “In allen sogenannten aromatischen Substanzen kann eine gemeinschaftliche Gruppe, ein Kern, angenommen werden, der aus 6 Kohlenstoffatomen besteht.” (In every so-called aromatic substance one common group, a kernel which consists of 6 carbon atoms, can be assumed) was contradicted by Erlenmeyer in the case of naphthalene,⁵ by Körner,⁶ and by Dewar for pyridine.⁷ In 1922 Crocker noticed that “aromatic structure is observed only in those combinations of elements which furnish *six* extra or aromatic electrons above those needed to complete a single-bonded ring”.⁸ He was thereby first to recognize the six aromatic electrons and in this way correctly described benzene, pyridine, thiophene, furan, and pyrrol. The circle, signifying the six aromatic electrons, was introduced by Armit and Robinson in 1925, but as they state that “the deletion of the central connecting bonds is more apparent than real”,⁹ it seems that they knew already from the beginning that their representation of polyaromatic hydrocarbons was flawed. In 1931, Hückel published the theory of cyclic $4n+2$ π -electron systems which forms the basis for Hückel’s rule for aromaticity.¹⁰ It was not until 1959 that Clar made the refinements to the resonance structures (Figure 1.1).¹¹

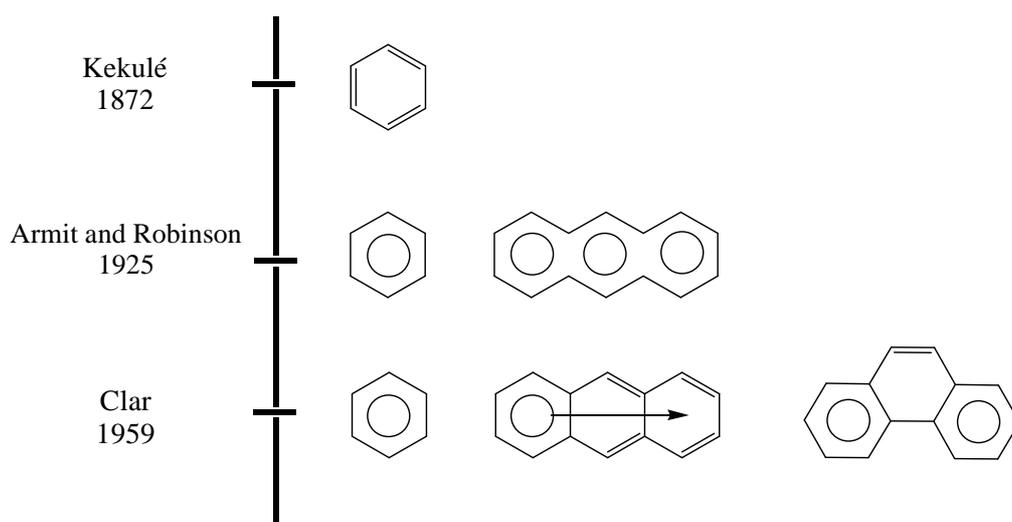


Figure 1.1. Evolution of resonance structures of benzene and polybenzenoid hydrocarbons from Kekulé to Clar.

The concept of aromaticity is to some extent intuitive. As a matter of fact the notion of “aromaticity” is controversial, difficult to understand or to explain in a few words. It implies that there is still a long way to go, and to dig, before we can conclude that this concept is of seminal value, useful in providing insight for the phenomenon. The core of aromatic nature is often defined by referring to a series of structural, energetic and spectroscopic characteristics, of which the following constitute the core: (i) a highly symmetric, delocalized structure involving six C–C bonds of equal length, each with partial double-bond character, (ii) enhanced thermodynamic stability, and (iii) reduced reactivity as compared to nonaromatic conjugated hydrocarbons.¹² Other properties that have been taken as symptoms of aromatic character are, for example, the down-field shift in proton NMR spectra, the exaltation of diamagnetic susceptibility, and a comparatively low reactivity.¹³ The counterpart of benzene is the antiaromatic 1,3-cyclobutadiene which, for example, shows localized double bonds instead of a regular delocalized structure with four C–C bonds of equal length.¹² There are many designations for aromaticity, but benzene is considered as the archetype of an aromatic molecule in all of the definitions. Soon after the designation of benzene as aromatic molecules, many characteristics of benzene were started to be used as benchmark to determine the aromaticity in other molecules. Often the degree of similarity of the characteristic between the molecule under study and benzene is then considered as a measure of Aromaticity. Aromaticity continues to be a topic in many studies associated not only with its relevance in chemistry, biology and technology, but also with the very concept itself. Indeed, despite many pioneering contributions on this issue, there is still a gap in our physical understanding of the nature of aromaticity.^{12,13,14} In the early twentieth century, Pauling and Hückel were the first to quantum chemically address the issue of benzene's structure and enhanced stability using valence bond (VB) and molecular orbital (MO) theory.¹⁵ In a VB-type approach, used by both Pauling and Hückel, the circular topology of benzene enables a resonance between the wave functions of two complementary sets of localized bonds, leading to an additional stabilization. In the MO approach applied by Hückel to the benzene problem, the enhanced stability of benzene compared, for example, to isolated or linearly conjugated double bonds, is attributed to an extra bonding contact (or resonance integral or interaction matrix element) in circularly conjugated hydrocarbons with $4n+2$ π -electrons^{15b,c} (a generalization to other than pericyclic topologies was later derived by Goldstein and Hoffmann).¹⁶

1.1.1. History and key advances

Since the isolation of benzene, the number of aromatic compounds has exponentially increased (See Table 1.1 for a summary of the main advances in the field of aromaticity). Before the end of the 19th century, the list was enlarged with benzene related monocyclic six membered rings. Then, the concept of aromaticity was extended to polycyclic rings such as naphthalene, anthracene, or phenanthrene and to rings with heteroatoms such as thiophene and pyrrole, and to annulenes and their ions e.g., tropylium cation. The work of Hückel helped to find a rule to discern between aromatic and non-aromatic compounds. With the concept of metalloaromaticity, aromaticity broke the confinements of organic chemistry. On the other hand, Heilbronner defined Möbius aromaticity, which follows exactly the opposite

behaviour of $4n+2$ rule. By means of theoretical calculations, Baird described a rule of triplet aromaticity which was experimentally validated by Wörner et al. in 2006.¹⁷ In 1978 Aihara introduced the three-dimensional aromaticity in boron clusters. Hirsch's rule allows one to predict the spherical aromaticity of recently discovered fullerenes and nanotubes.¹⁸ Finally, the most important recent breakthrough in the field of aromaticity took place in 2001, when Boldyrev, Wang et al., characterised the first all-metal aromatic cluster Al_4^{2-} . The properties of such molecules make them potentially useful for technical applications such as specific and very efficient catalysts, drugs, gas storage materials and other novel materials with as yet unimagined features. At variance with the classical aromatic organic molecules that possess only π -electron delocalization, these compounds present σ -, π -, and δ - (involving d -orbitals) or even ϕ - (involving f -orbitals) electron delocalization, exhibiting characteristics of what has been called multifold aromaticity. Figures 1.2 and 1.3 represent graphically the chronology of the advancement in aromaticity research.

Table 1.1. List of the key advances of the concept of aromaticity listed in chronological order.

Year	Main Contributors	Contributions
1825	Micheal Faraday ¹⁹	Isolation of benzene
1865	August Kekulé ²⁰	Cyclohexatriene benzene formula
1866	Ernlenmeyer ²¹	Reactivity basis for aromaticity
1922	Crocker ²²	Aromaticity sextet
1931	Hückel ²³	$(4n+2)\pi$ electron rule
1938	Evans, Warhurst ²⁴	Transition state stabilization by aromaticity
1945	Calvin, Wilson ²⁵	Metalloaromaticity
1959	Winstein ²⁶	Generalization of homoaromaticity
1964	Heilbronner ²⁷	Möbius aromaticity
1965	Breslow ²⁸	Recognition of aromaticity
1970	Osawa ²⁹	Superaromaticity
1972	Clar ³⁰	Clar aromatic sextet
1972	Baird ³¹	Triplet aromaticity
1978	Aihara ³²	Three-dimensional aromaticity
1979	Dewar ³³	σ -aromaticity
1979	Schleyer ³⁴	Double and in plane aromaticity
1985	Shaik and Hiberty ³⁵	π -electron distortivity
1985	Kroto ³⁶	Discovery of fullerenes
1991	Iijima ³⁷	Discovery of nanotubes
2001	Boldyrev and Wang ³⁸	All-metal aromaticity
2005	Schleyer ³⁹	d -orbital aromaticity
2007	Boldyrev and Wang ⁴⁰	δ -aromaticity
2008	Tsipis and Tsipis ⁴¹	ϕ -aromaticity

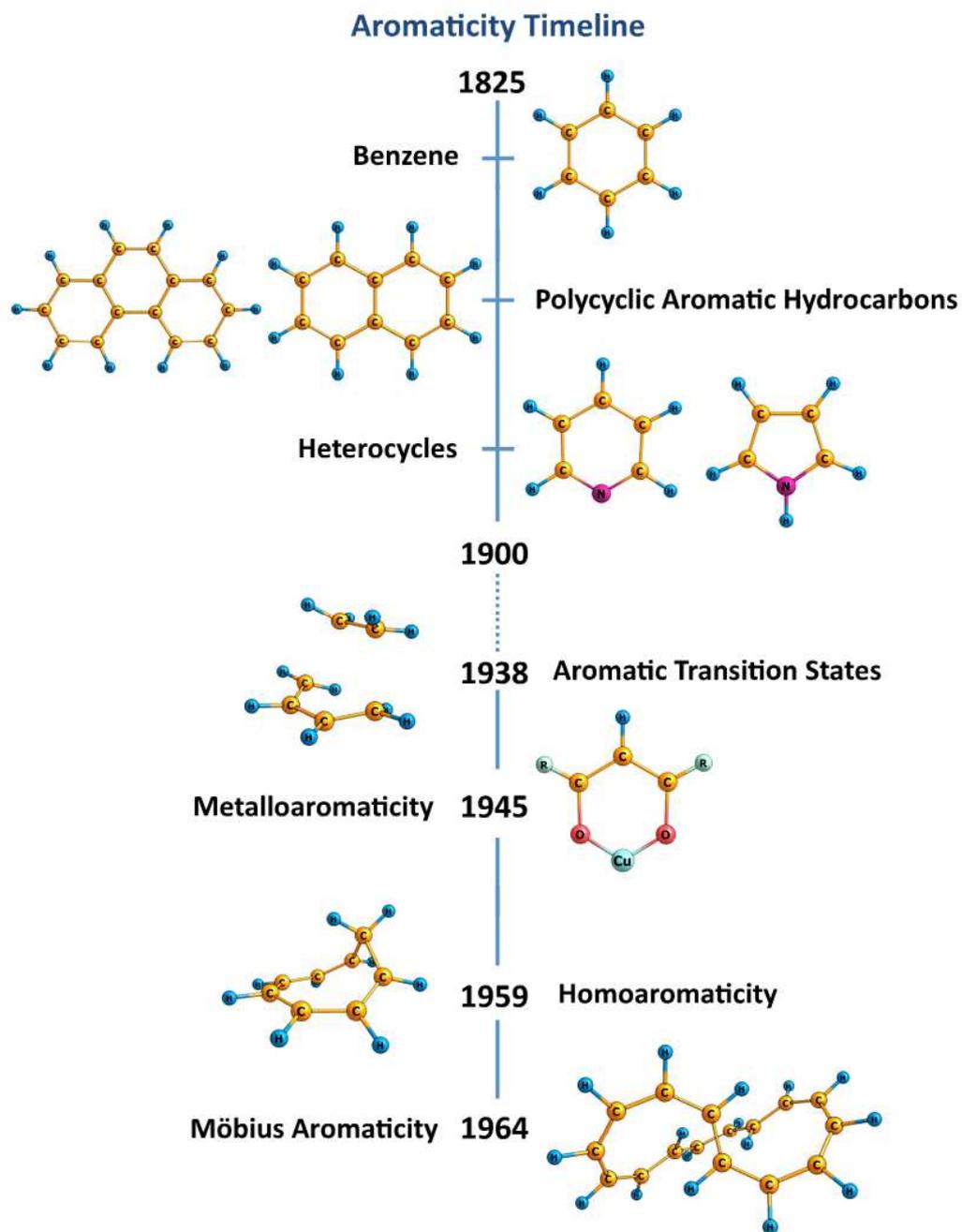


Figure 1.2. Most relevant advances of the concept of Aromaticity from 1825 to 1970.

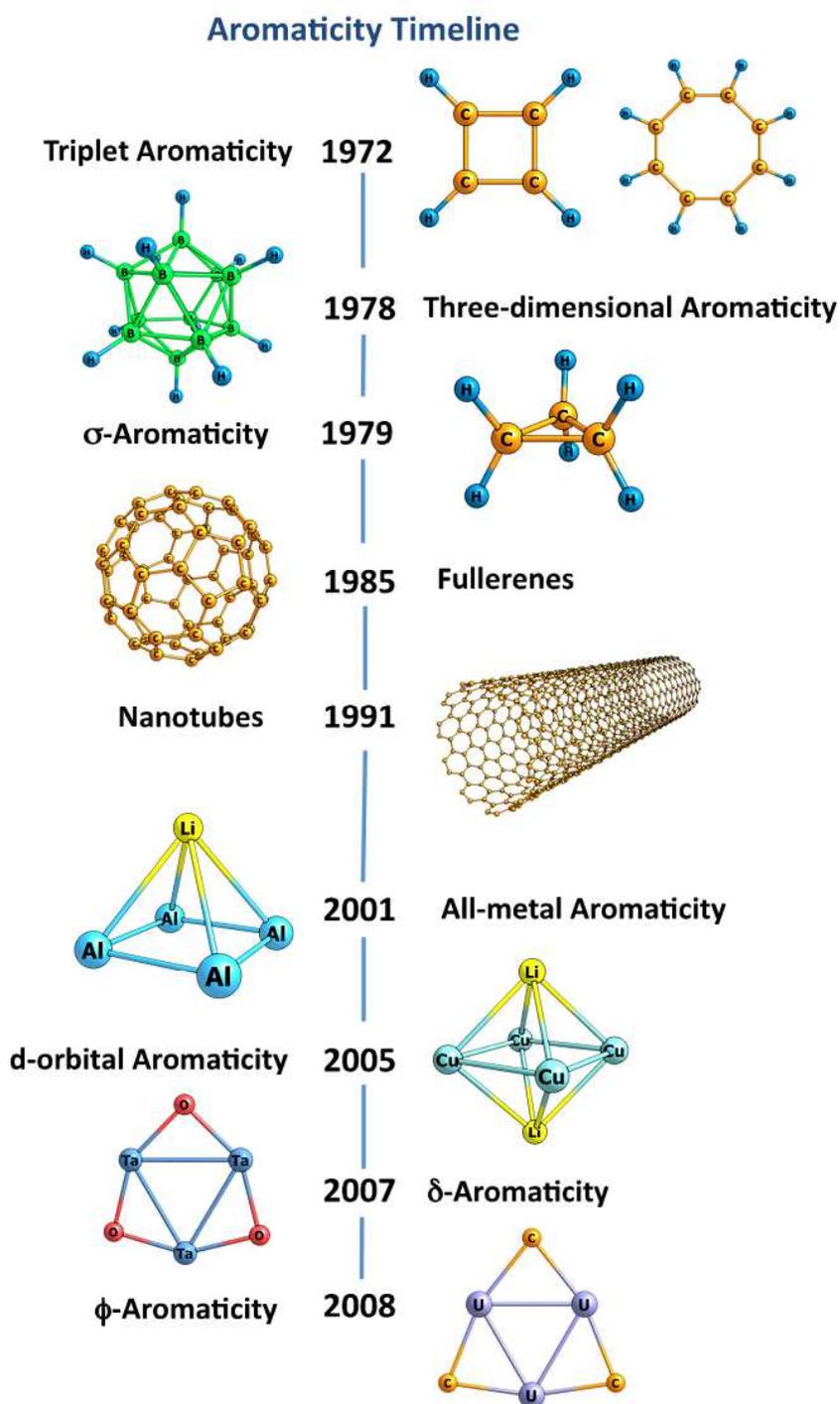


Figure 1.3. Most relevant advances of the concept of Aromaticity from 1970 to 2010.

1.1.2. Aromaticity in metal based systems

The concept of aromaticity is usually associated with organic compounds. The organometallic and inorganic aromatic species⁴² led the way to the discovery of σ -aromaticity⁴³ which was followed soon by the three dimensional aromaticity in certain spherical compounds.⁴⁴ The geometric, energetic and magnetic criteria are helpful to determine aromaticity in such species. However, the discovery of pure all-metal aromatic systems (AMAS) has made a prospect to the theoretical chemists due to the special nature of their chemical bonding leading to the existence of multi-fold aromaticity.⁴⁵ This discovery was followed by the searching of different novel all-transition metal aromatic as well as antiaromatic systems.⁴⁶ The presence of σ -, π -, and δ - or even ϕ -electron delocalization together, unlike classical π -electron delocalization in organic systems, enriches this special class of compounds. Besides, few of such systems drew attention to the scientific community due to the simultaneous presence of aromatic and antiaromatic ring current. The typical all-metal aromatic cluster Al_4^{2-} was reported to be a doubly aromatic system with the simultaneous existence of σ - radial- (σ_r -), σ -tangential- (σ_t -) and π -aromaticities. A number of metallo-aromatic compounds, e.g., Cu_3^+ ;⁴⁷ X_3^- (X=Sc, Y, La);⁴⁸ X_3^{2-} (X = Zn, Cd, Hg);⁴⁹ Hf_3 ;⁵⁰ Ta_3^- ;⁵¹ Au_5Zn^+ ;⁵² Cu_5Sc , Cu_6Sc^+ , Cu_7^{3-} and Cu_7Sc ;⁵³ M_4Li_2 (M = Cu, Ag, Au);⁵⁴ M_4L_2 and M_4L^- (M = Cu, Ag, Au; L = Li, Na)⁵⁵ etc. are also reported. This disparity of aromaticity in such metallo-aromatic systems, with their classical organic analogues, asked for a new definition which will resolve all the complexity and discrepancy to describe the phenomena of aromaticity.

1.2. Magnetism: History and Key Advancements

The first use of a loadstone compass can be found in China popular as *shao shih* or *tzhu shih*, which the Chinese meant loving stone more than four millennia ago. Then came the French word *l'aimant*, meaning attraction or friendship for magnet. The English word *magnet* came from the name of a region of the ancient Middle East, Magnesia, where magnetic ores were found. The amazing natural magic of magnets was known to the priests and people in Sumer, ancient Greece, China and pre-Colomban America. Zheng Gongliang in 1064, made a significant discovery that iron could acquire a resultant magnetization when quenched from red heat. Steel needles thus magnetized in the Earth's field were the first artificial permanent magnets. They aligned themselves with the field when floated or suitably suspended. A short step led to the invention of the navigational compass, which was described by Shen Kua around 1088. A lodestone sliced in the shape of a Chinese spoon was the lynchpin of an early magnetic device, the 'South pointer'. This 'South pointer' (Figure 1.4) were used for geomancy in China at the beginning of our era utilizing the property of the spoon turning on the base to align its handle with the Earth's magnetic field. Such permanent magnets are quite widespread in nature in the rocks rich in magnetite, the iron oxide Fe_3O_4 – which were magnetized by huge electric currents in lightning strikes.

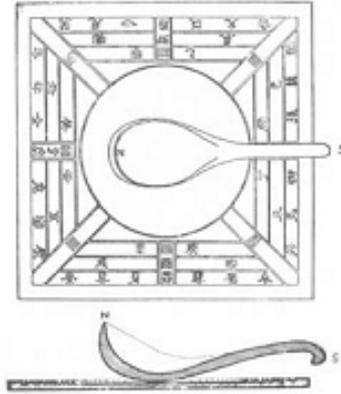


Figure 1.4. Some early magnetic devices: the ‘South pointer’ used for orientation in China around the beginning of the present era.

The Chinese are known to be the first to use abstract binary concepts such as yin/yang and male/ female, as well as understanding the concrete binary process of counting by the presence or absence of a bead in an abacus. But the development of a magnetic abacus, that is, a computer with binary magnetic information storage, took thousands more years to achieve. These magnetic memories were tiny toroids of ferrite that could be individually magnetized by simultaneous current pulses passing through two orthogonal wires. In this era of information technology the use of magnetic materials in tapes, floppy diskettes, and hard disks for the purpose of storing information are abundant in devices ranging from personal computers to supercomputers.

Magnetic materials are the backbone of progress of information technology in current days. Our seemingly insatiable appetite for more computer memory is satisfied by a variety of magnetic recording technologies based on nanocrystalline thin-film media and magneto-optic materials. Personal computers and many of our consumer and industrial electronics components are now powered largely by lightweight switch-mode power supplies using new magnetic materials technology that was unavailable 20 years ago. Magnetic materials touch many other aspects of our lives. Each automobile contains dozens of motors, actuators, sensors, inductors, and other electromagnetic and magneto-mechanical components using hard (permanent) as well as soft magnetic materials. Electric power generation, transformation, and distribution systems rely on hundreds of millions of transformers and generators that use various magnetic materials ranging from the standard 3% SiFe alloys to new amorphous magnetic alloys. Tiny strips or films of specially processed magnetic materials store one or more bits of information about an item or about the owner of an identification badge.

The magnetic properties of solids arise essentially from the magnetic moments of their atomic electrons. The quantum mechanics of electrons is described by Dirac equation which speaks that electrons have an additional degree of freedom, known as ‘spin’. The mathematical form of a “spin” is angular momentum and the genesis of magnetism is considered to be inherent within the interaction of such spins. The key advances in the field

of magnetism are given in Table 1.2. in chronological order. Magnetism can be divided into two groups. In one group, either there is no net spin moment or there is no interaction between the individual spin magnetic moments and each moment acts independently of the others. Congeners belonging to these groups are referred to as diamagnets and paramagnets respectively. In the other group, the individual moment couple to one another and form magnetically ordered materials. The coupling, which is quantum mechanical in nature, is known as the exchange interaction and is rooted in the overlap of electrons in conjunction with Pauli's exclusion principle. Most of the well known magnets are based on the compounds of iron, cobalt, nickel, gadolinium etc. which are ferromagnetic i.e. having unpaired spins in parallel orientation in their bulk state. The situation, where each spin is aligned antiparallel to its nearest neighbors, gives rise to antiferromagnetism. Metal compounds, MnO, MnF₂ or NiO are the archetypes of antiferromagnetic materials. In case, the numbers of antiparallel and parallel pair of spins are different or the antiparallely aligned spins are of unequal magnitude, a remnant magnetization develops in the material.

Table 1.2. List of the key advances in the field of magnetism in the chronological order.

Period	Dates	Icon	Materials
Ancient Period	-2000-1500	Compass	Iron, loadstone
Early modern age	1500-1820	Horseshoe magnet	Iron, loadstone
Electromagnetic age	1820-1900	Electromagnet	Electrical steel
Age of understanding	1900-1935	Pauli matrices	--
High-frequency age	1935-1960	Magnetic resonance	Ferrites
Age of Applications	1960-1995	Electric screw driver	Sm-Co, Nd-Fe-B
Age of spin electronics	1995-	Read head	Multilayers

1.2.1. Dimensionality and magnetic properties

An important branch of the molecular magnetism deals with molecular systems with bulk physical properties, such as long-range magnetic ordering. Molecular compounds with spontaneous magnetization below a critical temperature were reported during the eighties.⁵⁶ These pioneering reports encouraged many research groups in organic, inorganic, or organometallic chemistry to initiate activity on this subject, and many new molecule-based magnets have been designed and characterized. A tentative classification can arise from the chemical nature of the magnetic units involved in these materials— organic- or metal-based systems and mixed organic–inorganic compounds. The field of molecular magnetism is enriched with materials based on several families of magnetic metal complexes, such as the oxamato, oxamido, oxalato-bridged compounds and cyanide-bridged systems. The most extensively used spin carriers are 3*d* transition metal ions. The magnetic interactions between these ions are now well understood and enable the rational synthesis of materials. The heavier homologs from the second and third series have been envisaged only recently for the construction of hetero-bimetallic materials. In 1995 Olivier Kahn wrote a paper reviewing the magnetism of hetero-bimetallic compounds.⁵⁷ An important part of this review was devoted to finite polynuclear compounds, which can be considered as models for the study of exchange interactions. Magnetic ordering is a three dimensional property,

however, and the design of a molecule-based magnet requires control of the molecular architecture in the three directions of space.

1.2.2. Discrete molecules

One of the first high-spin molecules was prepared in 1988. It was a trinuclear linear CuMn₂ species synthesized by using [Cu(pba)]²⁻ as the core and [Mn(Me₆-[14]ane-N₄)]²⁺ as a peripheral complex.⁵⁸ However, no single crystal was obtained, and any structure in agreement with the magnetic properties was proposed for this species. The compound shows ferrimagnetic behavior with an irregular spin state structure resulting from the antiferromagnetic interaction between the peripheral Mn ions ($S_{\text{Mn}} = 5/2$) and the middle Cu ion ($S_{\text{Cu}} = 1/2$). The low-temperature magnetic behavior is the characteristic of a high-spin ground state equal to $S = 9/2$. Efforts were later made to obtain structural information for such species.⁵⁹ In this context it can be mentioned that Liao's group succeeded in isolating crystals of binuclear and trinuclear compounds with the Ni^{II} ion ($S_{\text{Ni}} = 1$).⁶⁰ These compounds were obtained by the reaction of CuL²⁻ (L = pba, pbaOH and opba) with NiL²⁺, L being tetraamine ligands, final compounds having formula (L Ni)CuL or (L Ni)₂CuL²⁺. These compounds have been magnetically characterized, and it is confirmed that they possess the expected ferrimagnetic behavior with an $S = 3/2$ ground state with a zero-field splitting. Another interesting example that can be cited here is by Ouahab and Kahn with the opbaCl₂ ligand and its Cu^{II} complex.⁶¹ The reaction of the Cu^{II} precursor with ethylenediamine, en, and Mn^{II} in the solvent DMSO led to an unprecedented trinuclear species Mn^{III}Cu^{II}Mn^{III}.

1.2.3. The importance of spin-nano magnets

The data storage industry is fast approaching the limit of the traditional bulk magnets used in computer hard drives. The ferromagnets that have been employed since IBM introduced the technology in 1953 are fundamentally limited, since the data becomes more volatile as the bit is made smaller. This has been termed the super-paramagnetic limit.⁶² Increasingly sophisticated methods are being used to dodge this limit, such as perpendicular storage⁶³ or using different substrates in disk construction. The issue is that as the domain of these bulk ferromagnets decreases, the potential for spontaneous demagnetisation (randomisation of spin orientation) becomes greater. Currently the bulk magnetic domain (which is made out of many small magnetic grains) is around the order of 100 nm.⁶⁴ Instead of continuing to evade this limit, it is possible to take a "bottom up" chemical approach for the construction of the magnetic bit. The ultimate goal of the nano-magnet is to create a molecule that is stable at room temperature, that retains its spin orientation for long periods and that can be easily read or manipulated. If this can be achieved then a new age of quantum storage is possible.

1.2.4. The single molecule magnet and the potential of quantum storage

The single molecule magnet (SMM) is one approach to create a molecular bit.⁶⁵ Each individual molecule is used to store data as the orientation of its electronic spin. The critical equation that governs the eligibility of an SMM takes the form

$$E = |D|S^2 \quad (1.1)$$

where E is the energy of the spin reversal barrier, S is the total spin of the system and D is the large component of the magnetic anisotropy. The energy barrier dictates the temperature up to which the spin retains its stability and thus controls the magnetic half-life of a nano-magnet. The issue of constructing large energy barriers is a chemical problem with two avenues to exploit; either the total spin of the system be large or the magnetic anisotropy could be increased. The current experimental trend is to construct ever larger clusters of inorganic molecules that contains multiple spin-unpaired electrons.⁶⁶ To create a molecule with a large paramagnetic ground state there are three main options, namely— (i) the use a hetero-metallic system where the metal spins are unbalanced, (ii) a homo-metallic system that contains an odd number of metal centres or (iii) a spin frustrated system. There is on-going research into the applicability of f -block elements⁶⁷ to attain ever higher ground state spins. A limitation of this approach is becoming apparent although the energy barrier scales as S^2 , the D tensor tends to scale as S^2 and thus renders the barrier increasing with spin of the order of S^0 .⁶⁸ A second factor in the construction of an SMM that must be considered is the magnetic anisotropy, D , which determines the spacing between the various spin states along the energy barrier.

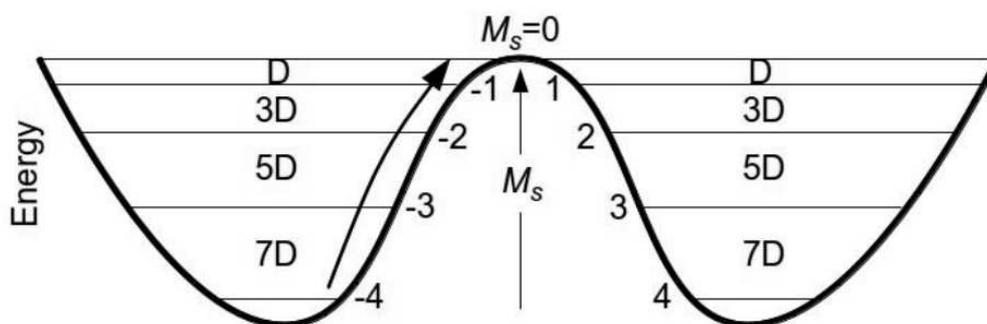


Figure 1.5. Diagram of the SMM energy barrier for an $S = 4$ system.

Here in Figure 1.5, M_s is the projection of spin in the S_z direction (the spin quantization axis). To create an SMM, D must be negative as this guarantees a ground state where the spin is all aligned along S_z and thus has a defined orientation for manipulation. As the molecule is excited and accesses higher lying M_s states, the spin is less orientated along S_z until it reaches the top of the energy barrier where $M_s = 0$ and is no longer orientated along that axis, at this point data would be lost. Nevertheless, a discussion of the quantum tunnelling mechanism is outside the work of this thesis. D is a difficult parameter to control

chemically as in inorganic systems it is dominated by spin-orbit coupling (SOC) and is extremely sensitive to ligand effects.

1.2.5. The role of theory in developing new magnetic molecules

Theoretical chemistry has some clear advantages in elucidating what is needed to create large D values. We are able to break D into its component factors of spin-spin interaction and spin-orbit coupling. Then, we are able to break down the spin-orbit coupling further and analyze the way its components influence its magnitude. Being able to calculate large SMMs is however out of the reach of pure wave-function methods due to their high computational cost; instead we must turn to density-functional theory (DFT), which has a much better scaling factor. Recently, Neese developed new methods of calculating the ZFS in a DFT framework; however it remains unclear if DFT in its current form is able to accurately model the coupling of the excited spin states needed to calculate D . Some analogy can be made to the electronic g-factor which is now readily studied in theory with a good degree of accuracy.⁶⁹ However, this is where the current limit of theoretical chemistry lies as the g-value only involves the coupling of electronic configurations of the same spin and the D value requires the coupling of excited states that can vary from the state of interest by $S \pm 1$. It is not clear that DFT is able to accurately model excited states of this nature as it is a theory of the ground state density. DFT studies so far show qualitative agreement with experiment.⁷⁰ The historic calculations of ZFS were done with ab initio methods.⁷¹

1.3. Objectives of the Thesis

The objective of the present thesis is to study the aromaticity of novel metal based system and the magnetic properties of metallo-organic complexes. The precise objectives of this thesis are defined in the following:

1. To study the aromaticity in metal based system and provide an insight about the onset of magnetism at the expense of aromaticity in such systems.
2. To study the effect of dimensionality on the magnetic exchange interaction of charge transfer transition metal complexes.
3. To study the effect of ligand-field on the magnetic anisotropy of the transition metal complexes.
4. To study the effect of external electric field in tuning the magnetic anisotropy of the metal base complexes.

Every chapter in this thesis is complete by itself; that is, it contains its own introduction, complete list of references, figures, tables, and interim conclusions etc.

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