1.1 A Nano History of Molecular Magnetism

The two terms *molecular* and *magnetism* that appear in the title of this book are here used in a well-defined scientific and technological frame; on the other hand, both of them are also often used, with different meanings, that influences how the scientific version is understood by specialists. Here we will not present a history of the concept of a molecule or a magnet, but we will highlight some general concepts in a scientific field that is developing fast. In order to be understood, it is necessary to make clear immediately what is meant by the title.

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Actually, there is a specification ("From transition metals to lanthanides") which is meant to indicate that the present book starts from what has been done in the last few years mainly using transition-metal ions. The novelty is the focus on lanthanides. Another possible subtitle could be "An f orbital approach to molecular magnetism".

Molecules, whatever the word means, are gaining space not only among specialists but also among lay people. The adjective "molecular" is attributed to an increasing number of scientific disciplines, and often the transition of a discipline to a molecular stage is a moment of its explosive development. Molecular biology, the branch of biology that deals with the chemical basis of biological activity, is a significant example. Chemistry is THE molecular science, covering the synthesis, reactivity, and functionality of matter down to the scale of 1 Å. There is no doubt that expressions containing "molecular" must be understood as a quality mark to the scientific approach, giving the impression of a set of activities investigating matter at the most fundamental scale, with as much detail as possible. The great success achieved so far in several molecular sciences is generating more and more molecular sciences. A short visit to Wikipedia shows as diverse substantives to go with "molecular," such as molecular pharmacology, psychiatry, therapy, endocrinology, microbiology, ecology, genomic, and so on. A tantalizing expression is "molecular foundry," but it has nothing to do with a workshop producing metal alloys with a molecular approach. In fact, it is a Department of Energy (DOE) program framed in nanoscience where the "foundry" provides researchers with instrumentation and expertise. Again, molecular implies something special.

Introduction to Molecular Magnetism: From Transition Metals to Lanthanides, First Edition.

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The present book will deal with molecular systems that possess magnetic properties, beyond the ubiquitous presence of diamagnetism, and the term *molecular magnetism* (MM) is to be understood as an indication of detailed studies at the molecular level, and as a coming of age of a discipline. There is no doubt that magnets came about much earlier than molecules. The latter term has a well-defined origin, both in time and space: the modern concept of a molecule appeared in France in the early seventeenth century, mole meaning a small mass. The English word "molecule" is documented in 1678, while Gassendi used it in 1658. The concept of molecule was worked out by Descartes as "bodies so small that we cannot perceive them and of which everybody is composed." With time, the modern concept of molecule emerged, and it became apparent that the properties of matter rely on the structure and reactivity of molecules.

Magnetism is much older, and the meaning of the word is controversial, associating it either with the name of a shepherd who discovered the attraction between iron and lodestone, or to the region, Magnesia, where the discovery was made. Additionally, there is evidence of an early use of compasses in China. At any rate, magnetism attracted attention because it allows action at a distance, as exemplified by the magnetic interaction between lodestone and iron, and their reciprocal attraction.

This action at distance puzzled mankind for millennia, and, since movement was associated with the existence in the lodestone of a soul. After all, we are still using the expression "animal magnetism" to indicate the attraction between people. Pliny gave a more material description of the coupling, but in 1600 Gilbert still interpreted the phenomenology with the soul concept: "Magnetic attraction arises because the Loadstone hath a soul." A major breakthrough came rather unexpectedly by joining magnetism and molecules, when Coulomb tried to imagine how a molecule could become polarized in the process of magnetization. But it was the key experiment by Oersted, in 1820, that opened new perspectives in the understanding of magnetism by showing that an electric current influences the orientation of a compass needle. In fact, Ampere suggested that currents internal to the material were responsible of the magnetism and that the currents must be molecular, that is, microscopic rather than macroscopic.

The contribution by Faraday to the knowledge of magnetism cannot be underestimated. In fact, he found that magnetic properties of matter are much more widespread than just lodestone and iron. He discovered that almost the totality of substances is weakly repelled by an applied magnetic field and called these substances *diamagnets*. A less numerous class of compounds was weakly attracted by a magnetic field and was called *paramagnets*. After discovering and naming diamagnetism and paramagnetism, Faraday conceived the concept of a magnetic field, and this view provided an explanation for the action at a distance that startled so much the ancients. A visualization of a magnetic field is shown in Figure 1.1, as obtained with a network of magnetic needles.

The other giant step toward understanding magnetism was taken by Maxwell who provided the mathematical frame that allowed the description of electromagnetism. Pierre Curie investigated the temperature dependence of the



Figure 1.1 The power lines as described by an assembly of dipolar magnets. [Source: Prof. M. Verdaguer – Personal Communication].

magnetization, discovering the law that carries his name. The French title of his thesis, published in 1895, translates "Magnetic properties of matter at variable temperatures". Three types of magnetic bodies are introduced and a list of compounds corresponding to diamagnets, paramagnets, and ferromagnets are reported with a few examples. The only molecules listed are oxygen and nitric dioxide, which are present among paramagnets (weak magnets).

But one of the main actors on the magnetic scene was still missing: the electron. It took some time between the suggestion by Stoney (1874), the discovery by Thomson (1897) working with cathodic tubes and the understanding that the same electron was responsible for the chemical bond. Let us assign the merit for this to Lewis, who suggested the electron pair bond and substantially improved the ingenuous formalism of chemical formulas.

The last step was the development of quantum mechanics, which provided the tools for describing the magnetic properties, starting a revolution that we are still observing. Many new concepts were introduced, and some of them have had a fundamental impact on magnetism, most important among them spin and exchange. Today, with the centenary of quantum mechanics approaching (if we can assign an official date), there is an ever-increasing usage of quantum concepts and quantum phenomena, not only for basic science but for applications as well. Concepts such as quantum tunneling, coherence, decoherence, entanglement, and superposition, are no longer the initiatic jargon of a few scientists but the basic tools of everyday scientific life of chemists, physicists, materials scientists, biologists, and engineers. At the same time, there has been a shift in the size and number of objects under investigation. Typically, one investigates an ensemble containing a huge number of molecules, and what is obtained is an ensemble average. On the other hand, more

and more experimental and theoretical tools allow addressing single molecules – a long way from Descartes and a complete paradigmatic shift.

We hope to have kindled some interest in a field that brings together the physical origins of magnetism with the chemical nature of molecules. One of the questions the book will try to answer is the following: does the above remark about a field acquiring a quality mark when becoming a molecular science also apply to MM?

1.2

Molecules, Conductors, and Magnets

Organic matter is often associated to electronic insulators but recently organic conductors have been synthesized and studied. Research has moved from molecular electronics to molecular spintronics. We will discuss the new exciting opportunities associated with the coexistence of electronic conduction with magnetic properties which provide unique opportunities for addressing individual molecules, storing, writing, and reading information in a single molecule, exploiting the quantum nature.

Molecular electronics is an example of a multidisciplinary approach as is well explained by R. Friend, a physicist who is one of the protagonists of molecular electronics:

One of the big opportunities in this science is that it crosses traditional divides between subject areas. There's communication between physics and chemistry and materials and divide physics. Managing that communication has been hard work, but it has been really rewarding, as well. It hasn't felt at all like the ordinary mode of activity for a research program in the physics department. In fact, I spend more of my time going to chemistry conferences than I do going to physics conferences. I find what I can pick up at chemistry conferences extremely valuable. I'm constantly trying to better understand what chemists are trying to do.

R. Friend

Magnetism is a property traditionally associated with metallic and ionic lattices. Till very recently, magnets were exclusively metals (Fe, Co, Ni, Gd), alloys (SmCo₅, Nd₂Fe₁₄B), or oxides such as magnetite (Fe₃O₄). This does not mean that magnetic molecules do not exist, O₂ being a clear example. But oxygen is a paramagnet which needs an applied magnetic field to work as a magnet and low temperature. The inorganic materials referred to earlier have permanent magnetization below a critical temperature (often called the *Curie temperature*) that is well above room temperature.

The idea of using organic molecules to make a new type of magnet, that is, an "organic ferromagnet," is a logical consequence of an argument of the following type: if molecules can yield unusual properties such as electrical conductivity, why should they not be magnetic? A gold rush toward this goal started in the 1970s, and it seemed to be successful when a nitroxide radical was reported to

be ferromagnetic at room temperature. Unfortunately, the initial claim was never confirmed. More accurate measurements show that the magnetization was due to iron impurities present in very low concentrations. The lesson was clear: when measuring weak magnetic systems, it is necessary to be extremely cautious. Even the random contact of the sample with a metallic spatula may pollute the sample. Indeed, shortly after such misplaced claims, it was discovered that nitroxides can yield purely organic ferromagnets (Kinoshita, 2004) but with a critical temperature in the range of 1 K, about two orders of magnitude smaller than what was hoped for. Further efforts were made, and the critical temperature increased to about 35 K in a few years (Banister *et al.*, 1996).

By looking around, it was soon realized that relaxing the condition "organic" to "molecular," a whole world was ready to be explored. Let us also have a look at this new world.

1.3 Origin of Molecular Magnetism

MM soon developed as a vital area of interdisciplinary investigation, which produced novel types of magnetic materials. The development of a joint interest among chemists (who moved to understand the difficult theoretical and experimental techniques needed to characterize the complex magnetic properties of the new MM) and physicists (who needed help to unravel the complex molecular structures that chemical ingenuity was able to produce). A NATO ASI was held in Italy in 1983, and the book that was written on that occasion can be considered as the birth of MM (Willet, Gatteschi, and Kahn, 1985). The title of the ASI was "Magneto-structural correlation in exchange coupled systems" and it stressed the need to work out simple rules to understand how to design molecules capable of interacting ferromagnetically with other molecules. This at least was the goal of the organizers, Olivier Kahn, Roger Willett, and one of the authors of this book. On the other hand, the physicists who took part in the event were interested in low-dimensional magnets and obscure objects such as solitons or the Haldane gap (Haldane, 1983). Were the chemists able to synthesize compounds that might show them? The ASI was a good catalyst for joint action, and MM took off (Coronado and Mínguez Espallargas, 2013; Ratera and Veciana, 2012; Wang, Avendaño, and Dunbar, 2011; Zheng, Zheng, and Chen, 2014).

Whithout any doubt MM comes from "Magnetochemistry" (Carlin, 1986). This is the use of magnetic measurements to obtain structural information, and can be done in several different ways. It is important to stress that it is not only a technical exercise as the next example will show, hopefully. Let us consider a Ni²⁺ ion: it has eight valence electrons that occupy the five 3d orbitals following the *Aufbau* principle, as shown in Figure 1.2. The free ion has two unpaired electrons and a corresponding magnetic moment. If the ion is tetra-coordinated, the degeneracy of the five 3d orbitals is removed. The limit coordination is square planar or tetrahedral. In Figure 1.2 is shown the pattern of d levels for the two cases.



Figure 1.2 Electron configurations for 3d⁸ in (a) spherical, (b) tetrahedral, and (c) tetragonal symmetry.

Nickel(II) in a tetrahedral symmetry has two unpaired electrons and the square planar D_{4h} has zero. Therefore, the former has paramagnetic susceptibility while the latter has diamagnetic susceptibility. A simple measurement of the magnetic susceptibility may decide the coordination geometry.

This kind of research was useful but not particularly exciting, except when the exotic quantum mechanical models were used by chemists for the first time. At the beginning, when magnetic measurements were performed at room temperature, the only safe information came from the comparison of the magnetic moment with that of the free ion. Implicit was the assumption that (i) ions did not interact with one another and (ii) the symmetry of the complexes was not guenched. The noninteracting model, which was sufficient for the simple Ni²⁺ system described above, was not working in many cases. Real life required to go beyond paramagnetism, to explore the interacting systems in which the magnetic properties require the presence of unpaired electrons that must weakly interact with other unpaired electrons. The simplest case of two centers, with one unpaired electron each, gives rise to a singlet and a triplet state, originating from the interaction whose separation must be of the order of 1-1000 K. Higher interaction energies lead the system to the limit of a true chemical bond, while below, the lower limit interactions are so weak to be negligible at all but the lowest experimentally accessible temperatures. We will now show with many examples how efficient the theoretical and experimental techniques are that allow the design of tailor-made magnetic molecules.

The goal of obtaining a molecular ferromagnet produced a complete change in the systems to be investigated. Well-behaved paramagnets gave way to interacting systems chosen, at the beginning, using the Goodenough (1958) and Kanamori (1959) rules which were suggested by Anderson's theory of magnetic interactions (Anderson, 1959). The rules were written in a language borrowed from the valence bond theory of the chemical bond, which was difficult to use for people with a molecular orbital (MO) background.

In the description of MM it is useful to characterize the interacting unpaired electrons with the nature of the half-filled orbitals s, p, d, and f. We will use this scheme extensively and hope to be convincing.

1.4 Playing with the Periodic Table

The intrinsic beauty of chemistry is that of creating new objects and a strong attraction for complexity. So new molecules were synthesized with 2, 3, and so on infinite magnetic centers, which showed interesting properties and waited for interpretation. The chemical way of thinking is intrinsically bottom-up, that is, going to the complex starting from the simple. MM is no exception. The procedure is, at the same time, a simple and a complex one. First of all, one has to choose the nature, size, shape, stability of reactivity, magnetic properties, and connectivity of the building blocks. These require the choice of the nature of the magnetic center. We will call the magnetic orbital the one that contains the unpaired electron, and one needs an efficient design to obtain a building of nice aspect. Molecules can make miracles, but they have severe limitations. The possibility of having bulk magnetic properties, for instance, ferro- or ferrimagnetism, requires an ordered array of 3d interaction. This proves to be difficult for molecules that are intrinsically of low symmetry, while it is easier for metallic and ionic lattices.

To determine the properties of the building blocks, let us start from using the magnetic orbitals. As stated previously, the magnetic orbitals are of p, d, and f nature. It is well known that p orbitals are external and reactive. As a consequence, magnetic organic compounds are generally unstable. On the opposite side, f orbitals are internal ones and very unreactive. In the middle stay the d orbitals. At the beginning of the MM era, the choice was for the p magnetic orbitals followed by d orbitals. The f orbitals were originally discarded, but in the last few years they have been intensively used for their unique properties. We will now have a look at the three types of magnetic orbitals, trying to understand the advantages and disadvantages as building blocks.

1.5

p Magnetic Orbitals

These are the most reactive and unstable orbitals. A pictorial view of selected molecules with electrons in p magnetic orbitals is provided in Figure 1.3. Among the building blocks we show, we can see nitroxides and nitronyl nitroxides, which have been studied as spin labels and spin probes (Jeschke, 2013) due to their good stability, which allows using them in solutions at room temperature. When used as spin probes, molecular moieties containing a paramagnetic group such as NO are



Figure 1.3 Examples of organic radicals: a) *p*-nitrophenyl nitronyl nitroxide; b) Verdazyl; c) 2,3,3,5-tetraphenyl-l H-1,2,4-triazol-1-yl. Hydrogen atoms are omitted for clarity.

selectively inserted into polymers and proteins (Tamura *et al.*, 2013). Electron spin resonance (ESR) spectroscopy is then used to get structural and dynamic information on the parts of the polymer or macromolecule. In both cases, the unpaired electron is mainly localized on the NO groups in a π orbital. The dimerization of the molecule through overlap of its π orbital or the π orbital of another molecule is hindered by the presence of bulky *t*-butyl groups (Figure 1.4a).

The interest in these systems is akin to the magnetochemistry approach outlined previously for the Ni compound: the magnetic properties are not relevant *per se*, but they provide structural information. But the organic ferromagnet revolution changed the interest in magnetic molecules focusing the attention on the magnetic orbitals and on their overlap. Figure 1.3 shows the formula of the first organic ferromagnet, which has a critical temperature of 0.6 K. The origin of the ferromagnetic behavior was interpreted as due to the overlap between positive and negative spin density regions in neighboring molecules (Takahashi *et al.*, 1991; Kinoshita, 2004). The lattice of magnetic centers is essentially three dimensional, as required for observing a transition to magnetic order. Unfortunately, the interactions are weak.

Organic ferromagnets were perhaps the first occasion for a stable collaboration between chemists and physicists in the field of magnetism, and the results were excellent. And with the results, the collaborations increased, producing even better results. The positive trend has been going on for 30 years now, and all indications seem to point to a bright future.

The other molecule of Figure 1.4 is a member of the family of TCNE, which in the reduced form TCNE⁻ is magnetic and can interact with other magnetic orbitals. A TCNE derivative with vanadium turned out to be a magnet at room temperature (Miller and Epstein, 1998). It is not purely organic, but it showed that



Figure 1.4 (a) Tetracyanoethylene (TCNE); (b) Tetracyanoquinodimethane (TCNQ).



Figure 1.5 The dithiadiazolyl radical.

molecules can produce three-dimensional magnets. Before this result, the first organometallic ferromagnet was reported, where the interacting magnetic centers were again TCNE, organic, and $Fe(C_5Me_5)_2$, that is, metal-organic (Miller *et al.*, 1987). Purely organic is the thioradical shown in Figure 1.5, which is ordered as a weak ferromagnet below 35 K: the highest temperature achieved so far is found in a sulfur-containing radical (Banister *et al.*, 1996). The difficulty with them is that they tend to interact antiferromagnetically, often giving a covalent bond and a diamagnetic adduct. Furthermore, they have a very small magnetic anisotropy, which is an appealing property for TM (transition-metal) and even more for rare earth (RE) molecular magnets.

An appealing property of organic radicals is that they can bind TM or RE ions, showing strong couplings. We remind that Lanthanides refers to fifteen elements from La to Yb. Rare earths indicates lanthanides plus Sc and Y. Since the metal ions often have more than one unpaired electron, or S > 1/2 as we will learn to say, also an antiferromagnetic coupling can yield a magnetic adduct. We will see several examples in the following (Miller, 2011).

So far, we have referred to organic radicals, that is, systems with unpaired electrons that contain carbon atoms. The unpaired electron density, however, is often mainly localized on N and or O atoms. But the criteria are simple: the smaller the size, the larger the coupling. Inorganic radicals such as superoxide, which have been largely neglected for molecular magnets, are now appearing in dedicated studies. An interesting feature is the possibility of controlling the intermolecular interactions by changing the cation. In any case, the effective magnetic moments of superoxide ions are larger than the spin-only value because of contributions of the orbital momentum (Dietzel, Kremer, and Jansen, 2004). Furthermore, it has been demonstrated that the zigzag arrangement of the half-filled superoxide orbitals can form a spin chain, with a superexchange pathway mediated by the p_z orbitals of the alkaline ions (Riyadi *et al.*, 2012).

Recently, another radical has been introduced in MM, namely $(NN)^{3-}$, which had seen some history in the framework of the nitrogen fixation studies. It was found early that lanthanides are very efficient in the step reduction of nitrogen, and more recent results have isolated compounds of formula shown in Figure 1.6 (Evans *et al.*, 2009). Of course, the radical needs protecting groups such as *t*-butyl to quench intermolecular reactivity.

Various spectroscopic techniques including ESR confirmed the presence of the radical. More details will be provided in Chapter 20.



Figure 1.6 Asymmetric unit of $[(ArO)_2(THF)_2Dy]_2(\mu-\eta^2:\eta^2-N_2)$, $(OAr = OC_6H_3(CMe_3)_2-2, 6)$. Hydrogen atoms have been omitted for clarity.

1.6 d Magnetic Orbitals

The d orbitals play a fundamental role in the field of MM. Their intrinsic features combined with the versatile chemistry of transition metals (Figure 1.7) offer the chance to synthesize compounds with a wide range of unusual magnetic properties. One class of systems that has been investigated for a long time for its peculiar magnetic properties is the so-called spin crossover (SCO) systems. It is based on the possibility of a metal to be stable in two coordination geometries which differ in the number of unpaired electrons. Let us consider an iron(III) ion in octahedral coordination. The 3d orbitals are split, with a set of three lying lower and a set of two lying higher, as shown in Figure 1.8. The former ones belong to the t_{2g} irreducible representation of the O_h group, while the latter to e_g . There are two possibilities to assign the five electrons to the five orbitals, one electron to each orbital, according to the configuration $t_{2g}^3 e_g^2$ or, alternatively all five electrons are assigned to the t_{2g} orbitals to give t_{2g}^5 .

The spin of the former configuration is 5/2, while for the latter it is just 1/2. The nature of the ground state depends on Δ_0 , that is, the separation of the two sets of levels. A large Δ favors the low-spin (LS) arrangement, while a small Δ favors the high-spin (HS) arrangement. Generally a molecule is either HS or LS. In a few cases, the molecule can have both states populated, at a certain temperature, giving rise to what is called *spin equilibrium* or *spin crossover*, an observation first made by Cambi in the early 1930s (Cambi and Szegö, 1931). In a very simple schematization of the process, the HS molecule is favored by entropy, while



 $\label{eq:Figure 1.7} \begin{array}{l} \mbox{Figure 1.7} & \mbox{Some relevant molecules} \\ \mbox{with nd magnetic orbitals. (a)} \\ \mbox{Dodecakis}(\mu_3\mbox{-}oxo)\mbox{-}hexadecakis}(\mu_2\mbox{-}perdeuteroacetato\mbox{-}O,O')\mbox{-}dodeca\mbox{-}magnese, \\ \mbox{perdeuteroacetato\mbox{-}O,O')\mbox{-}dodeca\mbox{-}magnese, \\ \end{array}$

(b) tris(N,N-diethyldithiocarbamato)-iron, (c) nonakis(μ_2 -fluoro)-heptadecakis(μ_2 -pivalato-O,O')-dioxo-hepta-chromium-di-vanadium; and (d) bis(2,2':6',2''-terpyridine)-cobalt.

the LS one is favored by enthalpy. Recalling that the t_{2g} orbitals are nonbonding (or weakly π antibonding) while the e_g are σ antibonding, it must be expected that the LS has shorter bond distances and is favored at low temperature. The HS–LS transition can be gradual or sharp, and can be accompanied by hysteresis. The transition can be monitored by measuring some property that is different for the HS and LS, such as the magnetic moment or the color. Typical curves are shown in Figure 1.9, exemplifying the behaviors mentioned above. Perhaps



Figure 1.8 Fe³⁺ d orbitals in octahedral environments of different strengths.



Figure 1.9 Temperature dependences of magnetic moment (μ_{eff}) of a typical iron(III) spin crossover compound. (Reproduced from: "Spin crossover iron(III) complexes", Coord. Chem. Rev., **2007**, *251*, 2606 by Nihei, M. *et al.* with permission from Elsevier B.V.)

the most important is the observation of thermal hysteresis, which makes the HS–LS bistable at a given temperature, with the actual status depending on the history of the sample. This is called *thermal hysteresis* because the variable causing it is temperature. Hysteresis is observed in magnets too, and it is caused by irreversible effects of the applied magnetic field. We will discuss at length the magnetic hysteresis in the following, because it is the basis for the implementation of devices – just think about the hard disk of your computer.

SCO properties have been reported for other ions in octahedral symmetry, such as iron(II), where the LS is diamagnetic and the HS has S = 2. These are perhaps some of the most currently investigated systems, and devices based on iron(II) have been tested for their use as memory cards. Iron(II) systems have also been found to undergo the so-called light-induced spin-state trapping (LIESST) effect. Flashing a laser on an LS molecule excites it to the HS form, as shown in Figure 1.10. There is a barrier for the molecule to revert to the ground state and the metastable HS state to survive at higher temperatures.



Figure 1.10 Magnetic and photomagnetic properties of a polycrystalline sample $[Fe(L_{222}N_5)(CN)_2]\cdot H_2O\ (L_{222}N_5=2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]$

octadeca-1(18),2,12,14,16-pentaene). (Reproduced from Costa, J.S. *et al.* (2007) with permission from The American Chemical Society.)

A milestone in the development of MM was the discovery of the magnetic properties of the so-called Mn₁₂ (Figure 1.7a). This cluster is a good example of zero-dimensional materials, and can be essentially regarded as a small piece of manganese oxide whose growth is blocked by the presence of carboxylates. It comprises 12 spin centers that are coupled to give a ground S = 10 state, with 8 Mn³⁺ having all the spins up and the 4 Mn⁴⁺ down. So far, there has been nothing particularly exciting. The real discovery was that, at low temperatures, the magnetization relaxes slowly and the molecule shows hysteresis like a tiny magnet. The phenomenon is called single molecule magnetism, and single molecule magnets (SMMs) have opened a new area of research (Aubin et al., 1996)., where quantum tunneling of the magnetization, a long-sought phenomenon in mesoscopic magnets, was observed. What had led to the failure earlier was the impossibility to control precisely the size of the particles. Since the tunnel relaxation scales exponentially, even small deviations in size of the particles hide the effect completely. This is particularly true for small-sized particles for which the monodispersity should be absolute. Molecules can do the job because they are all identical to each other. When the properties of Mn_{12} were reported, there was the feeling that a fundamental tile was laid.

1.7 f Magnetic Orbitals

Lanthanides or lanthanoids, or REs, are the elements with 4f valence electrons. This gives them a rather dull chemistry which shows up in the dominance of the +3 oxidation state, in great similarity in reactivity and solubility which made

their isolation a difficult task. It seems fit the description of a group of slaves, all similar to each other and who do not dare to show differences. But it is only a false impression; under the uniform, they show rich and different dresses. Apart from the metaphor, the magnetic properties of Ln are unique because they have contributions from the spin and orbit motion of the electrons. The spin motion is, without fantasy, equal in the three directions in space, monitored by a proportionality constant between the intensity of the applied magnetic field and the generated magnetic moment, $g_{e} = 2.0023$. The orbital momentum, on the other hand, is different for different electrons, and it is in principle different in the different directions in space. Measuring the magnetic properties provides structural information, and this opportunity has been widely used in what can be described as the beginning of the molecular RE saga.

An important step was associated with the discovery that the presence of lanthanide complexes in solution induces shifts in the NMR spectra and increased resolution. In recent years, the discovery that molecular clusters behave as tiny magnets at low temperature has opened the stage of SMMs. The following steps were the extension to polymers, single chain magnets (SCMs), and, in the opposite direction, to single ion magnets (SIMs). With some delay compared to TM ions, lanthanides became one of the focal points of molecular spintronics where they provided the advantages of their unquenched orbital momentum. This new class of experiments requires a theoretical background, which is not trivial. It was worked out in the 1960s when the computer era was at the beginning and symmetry group theory was routinely used in a sophisticated way to reduce the size of the matrices required to calculate the properties. It is a very elegant way to write, and we recommend the interested reader to read Orbach's paper in which he introduces the magnetic relaxation mechanism which now is called after his name (Orbach, 1961).

1.8

The Goals of Molecular Magnetism

Classifying molecular magnets using the nature of the magnetic orbital is one possibility, but there are other options based on the definition of appealing goals that may develop toward exciting applications. As an example, SCO systems started as basic science, but now are pursued for magnetic bistability applications.

The development of strategies for organic (molecular) ferromagnets has produced two samples that are exciting achievements for basic science but rather removed from the expected applications. For instance, there were expectations for soluble magnets, which remain unachieved. The next appealing goals were bound to molecular spintronics, which developed in parallel to the development of spintronics and had a flash start with a Nobel Prize (Fert, 2008). The molecular aspects form a well-suited background in the so-called SMMs, which had been independently developed after a serendipitous discovery.

The current last step is toward quantum computing, that is, the use of quantum effects for developing a new type of computing. After many attempts to develop properties in hostile environments for molecules, the quantum realm appears to be favorable for molecules (Leuenberger and Loss, 2001).

1.9 Why a Book

In the last few years, there has been an exponential growth in interest on the magnetic properties of lanthanides. Their derivatives have found applications in new technologies widely diffused in our lives. Having worked in the field of magnetic properties of lanthanide ions for more than 30 years, we have personally experienced the difficulties inherent to the comprehension of these properties and dreamed to present a book that explains in a simple way the physics hidden beyond the guantum mechanical approaches. Since nobody had so far produced such a book, we decided to try to produce one ourselves. The last sentence is not guite correct; there are excellent edited books (Miller and Drillon 2006). Of course, the treatment of the matter for an edited book is more detailed, and we feel that there is room for both approaches. The idea was to keep the book short, using quantum mechanical approaches in a semiquantitative way, avoiding demonstrations as far as possible. But when we started writing, we realized that p, d, and f orbital systems are mixed in such a way that it is impossible to speak of one leaving out the others. So the menu changed for better food, becoming a general introduction to MM from the point of view of lanthanides. Of course, there is an overlap with Olivier Kahn's Molecular Magnetism, a perfect book (Kahn, 1993). But we chose the topics to have minimum overlap with that.

The new book has obviously some overlap with *Molecular Nanomagnets* by J. Villain, R. Sessoli, and one of us (Gatteschi, Sessoli, and Villain, 2006, GSV in the following). However, we feel that the focus on Ln of the present book will ensure the correct coverage.

The other points to critically discuss when starting to write a book are the following: Is it worthwhile? Is the area covered by other books? At which audience is it aimed - the expert, the beginner, chemists, physicists, or others? We could continue.

After this analysis, we decided that there should be room for a unitary book covering the main features of MM without trying to cover all the topics. We tried to integrate a historical approach, especially for the topics where we have given a personal contribution to the field, to a readable treatment of recent developments.

The conclusions are condensed in the title: we want to give an introductory coverage of MM but will do that from the point of view of Ln. There will be paragraphs dedicated to organic and TM, but there will be no attempt to cover these areas in detail. We will use them as an introduction to Ln-based MM.

16 1 Introduction MCE What MRI Else SCO SMM р 1 D οD COOF SIM MM d 2-3 D MOF SCM MS7 DF1 OIP

Figure 1.11 Scheme of the structure of this book as explained in the text. For acronyms, see Appendix A.

1.10 Outlook

The first step is to produce a graphic outline of the contents of the book shown in Figure 1.11.

The hexagonal tiles correspond to research areas, starting from the central one, which refers to *magnetochemistry* as the common origin. The first ring of growth reminds us of the relevance of the dimensionality and of the nature of the magnetic orbitals. Finally, ring 2 tries to highlight the main research areas.

We will try now to inform the reader on how the book is organized, giving the opportunity to decide whether to bypass chapters that he or she is already familiar with.

Chapter 2 deals with the electronic structures of the free ions, stressing the role of spin–orbit coupling and the differences between TM and Ln. The effect of applying a magnetic field on the spherical ions is also included.

Chapter 3 covers the coordinated ions working out the spin Hamiltonian approach to the energy levels trying to make clear the formalism and comparing the most common parametrization schemes. A series of compounds of Ln *aquo* ions are used as a test of magnetostructural correlation, also taking advantage of the angular overlap model that will be shown to be a useful tool for justifying the angular dependence of the bonding parameters. There is an introduction to the importance of magnetic anisotropy, which will be the leitmotiv throughout the book.

Chapter 4 describes in a very synthetic way some chemistry of the main family of derivatives whose magnetic properties are analyzed in depth in the other chapters of the book. The chapter is organized according to type of ligands: pyrazolylborates, phthalocyanines, cyclopentadiene and cyclooctatetraene, polyoxometalates, diketonates, nitronyl nitroxides, carboxylates, and Schiff bases.

Chapter 5 presents the basic magnetic properties of the individual magnetic building blocks, the anisotropy, and the strategies to design them correctly. The basic Curie and van Vleck equations are introduced, and their effects on the magnetic data of Ln are discussed with some suitable examples; particular attention is given to the origin of the anisotropy, of the second, fourth, and sixth order.

Chapter 6 titled "Molecular orbital of isolated magnetic centers" introduces the MO approaches to the calculation of the magnetic properties of mononuclear compounds. The goal is to provide a minimum amount of information on the *ab* initio and DFT (density functional theory) techniques, while trying to define all the acronyms that make theoretical papers difficult to read. The two theoretical models are compared, and pedagogical examples are worked out with a TM in a very simple coordination environment and with Ln to obtain information on the magnetic relaxation showing the power of the method If one is asked which have been the most important theoretical and experimental techniques which in the last years have allowed breakthroughs in the developments in MM then computational chemistry would certainly be a top scorer. If one is asked which have been the most important theoretical and experimental techniques which in the last years have allowed breakthroughs in the developments in MM then computational chemistry would certainly be a top scorer.

Chapter 7, titled "Towards the molecular ferromagnet", is a central one, because it focuses on the description of the interaction between the magnetic building blocks, a key factor for designing molecular magnets. The treatment is made at the spin Hamiltonian level. The title of the chapter highlights one of the strategies that has had a stimulus for designing more and more complex arrangements of molecular magnetic building blocks to build a molecular magnet characterized by permanent magnetization. In fact, learning what the conditions are to induce a transition to magnetic order is stringent and difficult to meet with molecular building blocks. Complementary strategies aiming at building ferrimagnets, weak ferromagnets, and so on, are discussed, highlighting the interest for finite-sized molecular magnets.

Chapter 8 describes the MO treatment of exchange and superexchange interactions first introduced by Anderson, moving from semiempirical methods toward state-of-the-art ab initio and DFT calculations. We briefly comment on the techniques needed for discussing the MO approach to weakly coupled systems, such as the broken symmetry approach. We treat in some detail copper acetate because it has had an important role in the understanding of magnetic interactions.

Chapters 9 and 10 show real-life examples of the design, synthesis, and investigation of properties of compounds containing similar and different magnetic orbitals. In particular, Chapter 9 is about interactions involving p orbitals, highlighting the McConnell models, while Chapter 10 covers the d-d interactions not only 3d but considering heavier TMs. Interactions involving f orbitals are dealt with considering Gd-Cu derivatives.

Chapter 11 is the introduction of dynamics in the magnetic properties, or the revolution of Mn₁₂. Spin-lattice and spin-spin relaxation are introduced, together with the quantum tunneling mechanism and the interaction with the thermal bath.

Chapter 12 gives examples of SMM mainly based on TM, not covering in detail the literature but providing a critical view of what has been done and what

remains to be done. Chapter 13 does the same for f-based systems. Particular emphasis is given to the SIMs, which are typical of f electrons. This is one of the hottest topics in MM. Important properties including quantum effects are discussed in the frame of two classes of materials defined by Ln phthalocyanines and polyoxometalates.

Chapter 14 presents SMMs based on f magnetic orbitals, and Chapter 15 covers SCMs based on Ln. The discussion covers far-reaching arguments such as non-collinear axes and chirality, which are present also in other classes of compounds.

Chapter 16 is dedicated to Dy in order to cope with the wave of reports on this magic element.

In a sense, Chapter 17 is the opposite, focusing on individual molecules organized on surfaces and addressed with electric and magnetic fields. These are the hot topics where molecular spintronics, quantum computing, and so on, are covered together with the development in quantum computing (Chapter 18).

Chapter 19 underlines the conditions required to control the growth of 3D structures and covers the developing field of clusters of increasing size going to the limit which has so far been achieved with some indications of the techniques to analyze their magnetic properties. The strategies for 2D clusters are covered in the last section.

The final chapters cover the most used experimental techniques, namely ESR, NMR, some more or less direct application of molecular.

1.11 The Applicatio

The Applications of Ln

Before closing this introductory chapter, it may be instructive to have a brief look at the main applications of REs, whose compounds now dominate a huge market in continuous expansion. The first industrial compounds involving lanthanides were produced by Carl Auer von Welsbach (the discoverer of neodymium and praseodymium) at the beginning of twentieth century. As he was already selling the gas mantle for obtaining a more intense gas light, he had problems in finding applications for all REs that remained after the treatment of monazite sands to extract thorium for his mantles (99% Th to 1% Ce). He started the production of "mischmetal" or Auer metal, which was a large success as a lighting flint. It was an alloy consisting of about 50% cerium, 25% lanthanum, 15% neodymium, 10% other RE metals, and iron which was added to increase the strength of the alloy. Mischmetals with similar composition are also used as deoxidizer in various alloys, to remove oxygen in vacuum tubes, sulfur impurities, and as an alloying agent with soft metal such as magnesium, because it provides high strength and creep resistance.

In the following years, the use of lanthanides increased continuously and, despite their cost and very similar chemical behavior, each of the 4f elements found a specific niche, making it fundamental for a number of different technological applications.

Their peculiar magnetic properties have been exploited in the production of alloys such as $SmCo_5$ and $Nd_2Fe_{14}B$, which constitute the majority of the permanent magnets. Molecular compounds are, today, irreplaceable contrast agent in MRI (magnetic resonance imaging). Moreover, the 4f ions play a relevant role in high- T_c superconductors.

Moreover, they are very versatile, offering the possibility to find the same element involved in very different applications. For example, Lanthanum is used to produce high refractive index glass, flint, hydrogen storage systems, battery electrodes, camera lenses, fluid catalysts, and cracking catalysts for oil refineries.

Their optical spectra show in visible and UV regions very sharp absorption lines, much sharper than those of usual transition elements, and this feature makes them essential in all application where bright colors are required. They have been used for a long time in staining glass and ceramics and, later to produce phosphors in classical cathode ray tube (CRT) monitors and TV devices. The possibility of using them in preparing OLED (organic light-emitting diode) screens is currently under study. Because of their optical properties, lanthanides are widely used in lasers (i.e., Nd:YAG) and as dopants in optical fiber amplifiers; for example, erbium is introduced in amplifiers used as repeaters in the terrestrial and submarine fiberoptic transmissions. Some lanthanide iron garnets are fundamental to producing tunable microwave resonators.

Another peculiar property derives from their ability to absorb neutrons and, therefore, they are used in nuclear reactors in control rods and as shielding and structural materials. For safety reasons, they have substituted thorium to improve the welding properties of tungsten.

As is shown in the following table, approximately 40% of the 125000 tons of lanthanides produced in 2010 is employed in producing magnets and catalytic products. The fastest growing markets are permanent magnets, rechargeable batteries, phosphors, and polishing agents.

Application	Percentage
Magnets	25
Fluid cracking catalysts	15
Battery alloys	14
Polishing powder	14
Metallurgical	9
Auto catalysts	7
Glass additives	6
Phosphors	6
Others	4

Ln compounds are widely used in heterogeneous catalysis as metals, but more molecular systems such as triflates (they are considered among the most

promising catalysts for the so-called "green chemistry") and metallocenes are also widely used in homogeneous catalysis. The latter ones are under investigation also for their magnetic properties but, as far as we know, there is not much overlap between the two types of investigation. It might be useful to crash the barrier by importing magnetic techniques.

The largest end user of REs is the permanent magnet industry. This segment represents about 25% of total demand and is expected to grow to 30% by 2015. Lanthanides are in high demand due to their strength, heat resistance, and ability to maintain their magnetism over very long periods. Magnets made from RE elements such as neodymium, praseodymium, and dysprosium are the strongest known permanent magnets. Their higher performance and smaller size enables many miniature applications, such as personal electronic devices (smart phones, ear buds, MP3 music players). A miniature magnet made with neodymium causes the cell phone to vibrate when a call is received. Capacity utilization is one of the biggest challenges in the wind energy sector. Replacing gear-driven turbines with powerful direct-drive permanent magnet generators can increase efficiency by 25%, and some very large turbines require two tons of RE magnets.

One of the key features that determine the excellent behavior of SmCo_5 and $\text{Nd}_2\text{Fe}_{14}\text{B}$ as hard magnets is lanthanides magnetic anisotropy. The latter has been studied under many conditions to optimize the performance of the material. It must be recalled that the high-performance materials are used in many different ways, ranging from cell phones to wind mills and the automotive and aerospace industries. REs provide the so-called single ion anisotropies (magnetocrystalline anisotropy) which are associated with crystal-field and spin–orbit coupling. These factors have their influence on the orbital momentum of magnetoelasticity and magnetoresistance. In order to understand the differences and similarities between inorganic and molecular magnets, it will be necessary to introduce more detailed models. We are convinced that the bottom-up approach to magnetism can be extremely useful, and we will try to underline it whenever we will find some complementary approach between bottom-up and top-down schemes.

Applications can give rise to problems originating from the availability of the materials. Rare earths have a discouraging name, but in the practice they are actually rather abundant. The problem mainly lies in the fact that there are no mines containing one single metal, but ores contain many different metals, with extremely similar chemical properties.

Associated with the previous considerations is the world distribution of resources, which is far from uniform. Reserves are widespread, but the machinery and sophisticated equipment needed for the viable extraction of the elements from the ores are only available in a few countries such as the United States, India, Commonwealth of Independent States, and, above all, China. Owing to the less stringent environmental policies, in 2010, 94% of the global production of REs came from Chinese mines. In the last few years, the demand of lanthanides has been growing at 9-15% a year and the spreading of technologies strictly connected with RE derivatives is creating supply criticality especially for Nd, Dy, Eu, Tb, and Y.

1.12 Finally SI versus emu

Apparently, there should be no doubts on the units to be used in magnetism. The ninth General Conference on Weights and Measures in 1948 on taking the final decision on the electrical units indirectly defined the magnetic ones. According to the expression of Lorentz force, a particle of charge q moving with velocity v in the presence of an electric field E and a magnetic field B will experience a force f given by

$$f = q(\boldsymbol{E} + \boldsymbol{\nu} \times \boldsymbol{B})$$

Therefore, the electric and magnetic fields can be expressed in terms of the basic quantities of mass, length, time, and current. According to the *Systeme International* (SI), the units of *E* and *B* are, respectively, Newtons per coulomb (N C⁻¹), and Newtons per coulomb per meter second (N C⁻¹ m⁻¹ s), where a coulomb (C) is an ampere-second. The latter can be expressed either as kilogram per square second per ampere (kg s⁻² A⁻¹) or tesla (T). The tesla is a rather big unit. The largest continuous field ever produced in a laboratory is 45 T and the field at the Earth's surface is a few tens of microtesla.

Everything looks fine and clear, but in everyday practice things are different because in most reports on magnetism centimeter – gram – second (cgs) units are still used. Sometimes it is even worse, and mixtures appear, so that it is possible to find in the same paper "tesla" used when fields are strong and "oersted" when they are small. This is misleading not only because the two units belong to different systems but also because tesla measures the magnetic flux intensity (*B*) and oersted the magnetic field strength (*H*). Just to be more precise, in the cgs system the two quantities are related by the expression

$$B = H + 4\pi M$$

where *B* is measured in gauss, *H* in oersted, and the magnetization (*M*) in electrommagnetic unit per cubic centimeter (emu cm⁻³).

Through the book you will find the same mixed notation as is usually used in the literature. In an attempt to make reading easier, we report here the most useful conversion factor between SI and cgs units and a complete table in Appendix B.

1 T	=	10 kG
$1 {\rm kA} {\rm m}^{-1}$	=	12.57(≈12.5) Oe
$1\mathrm{A}\mathrm{m}^2$	=	1000 emu
$1\mathrm{MJ}\mathrm{m}^{-3}$	=	125.7 MG Oe
$1 { m A} { m m}^2 { m kg}^{-1}$	=	$1 \mathrm{emu}\mathrm{g}^{-1}$
1 G	=	0.1 mT
1 Oe	=	79.58 (\approx 80) A m ⁻¹
1 emu	=	$1 \mathrm{mAm^2}$
1 MG Oe	=	7.96 kJ m ⁻³
$1 {\rm kA} {\rm m}^{-1}$	=	$1\mathrm{emu}\mathrm{cm}^{-3}$

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