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# Molecular magnetism, status and perspectives

Dante Gatteschi [a,*], Lapo Bogani [a], Andrea Cornia [b], Matteo Mannini [a],
Lorenzo Sorace [a], Roberta Sessoli [a]

[a] La.M.M., Department of Chemistry and INSTM RU, Università di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy
[b] Department of Chemistry and INSTM RU, Università di Modena e Reggio Emilia, Via G. Campi 183, 41100 Modena, Italy

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## Abstract

A short review is made of molecular magnetism, trying to discuss what is alive and well, with perspectives for the future. All the main fields of activity are mentioned, ranging from the so-called spin cross-over systems to the quest for organic (molecular) ferromagnets. Particular attention is devoted to some of the recent advances in these fields, highlighting also the opportunities for the development of applications. Low dimensional magnets are perhaps the best opportunity to use molecules, and the status of single-molecule and single chain magnets is discussed. The last part is devoted to the organization of magnetic molecules and to the development of techniques which allow to measure the magnetic properties of thin layers and, in perspective, of single molecules.

*Keywords:* Molecular magnetism; Nanomagnets; Organic magnetism; Multifunctional materials; Molecular spintronics

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## 1. Introduction

Molecular magnetism is a recently developed research area that targets the design, the synthesis and the investigation of the magnetic properties of molecular materials. It is not limited to this, however, and it is actually extended to every magnetic material that can be obtained by using molecular approaches. The start of molecular magnetism can be dated from the attempts made in the late 1970s of last century to obtain organic ferromagnets. The idea was that since organic matter could show metal-like conducting properties there should be the possibility to create ferromagnetic materials using organic building blocks. As we will see room temperature organic ferromagnets have proven to be much more difficult to obtain than organic conductors and semiconductors and after around 30 years this task has not been achieved yet. This failure of the prefixed goal, anyway, has not been a catastrophe for the field. The idea of systematically using molecules to give rise to new magnetic properties has actually been a very productive one, and has catalysed the interaction of chemists and physicists giving rise to a fertile interdisciplinary field. Important results have been obtained, especially in what can be called molecular nanomagnetism, because the peculiarities of molecular structures have allowed to monitor the interplay of classical and quantum effects in magnetism.

The goal of the article is that of highlighting some of the milestones of molecular magnetism. An in depth coverage of all the aspects of the field will not be attempted, and we will instead try to collect, according to the authors' sensitivity, the main research areas where molecular approaches have given more added value. In fact this is intended as a contribution to a book of proceedings, and starts necessarily from the presentation that was made in Peñiscola at ISCOM2007. Important books or authoritative reviews covering some, or all, the aspects of molecular magnetism are available, and the interested reader is addressed to them when looking for completeness [1].

The organization of the paper is the following. We will start from the oldest example of molecular magnetism, *i.e.* spin cross-over systems, which were discovered in the 1930s by Cambi [2] in Milan, and after more than 70 years is still alive

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* Corresponding author. Tel.: +39 0554573285; fax: +39 0554573372.
*E-mail address:* dante.gatteschi@unifi.it (D. Gatteschi).

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and well. Then we will cover what can be called "the quest for the organic ferromagnet", highlighting the difficulties associated with using molecules to build three-dimensional networks of ferromagnetic interactions. We will then move to two fields in which molecular approaches offer some definitive advantages: zero-dimensional magnets, with particular emphasis on single-molecule magnets (SMM), and one-dimensional magnets, with special focus on single chain magnets (SCM). The last step will bring us to the present and the future with the organization of molecules on suitable substrates with the goal to move to the challenging area of molecular spintronics.

## 2. Spin cross-over and related systems

Spin cross-over is an accepted shorthand description of isomeric systems which differ only for the spin value. A well-characterized class of spin cross-over compounds is that of $d^4$–$d^7$ octahedral compounds which can exist either in a high- or a low-spin ground state depending on the strength of the ligand field, LF, which splits the d orbitals in the $t_{2g}$ and $e_g$ manifolds. Strong LFs favour the low-spin state, LS, while weak fields favour the high spin state, HS [3,4]. For intermediate fields the two configurations have comparable energies, and they can be in equilibrium. HS has larger entropy and is favoured at high $T$, while LS, which has fewer electrons in the $e_g$* orbitals and consequently shorter bond lengths, is more stable at low $T$. The LS → HS transition may occur gradually or abruptly depending on the vibronic interactions between the molecules. In some cases the transition is accompanied by a thermal hysteresis that has allowed the design of information storage devices based on spin cross-over materials [5].

The LS → HS transition can be induced also by pressure and by light. The latter is the so-called light-induced excited spin state trapping (LIESST) effect [6,7], which allows inverting the populations of the low and high spin states at low temperatures. This is certainly an exciting phenomenon, which in principle opens the way to many possible devices exploiting the light-induced switching of molecular properties. The main limitation, however, is that it typically occurs only below 50 K, because thermal energy accelerates the decay from the excited high spin state. The relaxation rate has been associated to the difference in energy between the zero phonon levels of the two forms and to the difference in bond distances in the two forms. The relaxation can occur both through an Arrhenius mechanism and a phonon assisted tunnelling.

Several attempts have been made to increase the working temperature, in particular by irradiation in the thermal hysteresis loop. Bonhommeau et al. [8] reported that by irradiating $[Fe(pyrazine)Pt(CN)_4]$ at 532 nm with 8-ns pulses it is possible to induce HS → LS or LS → HS transition depending on the position in the hysteresis cycle. This result has been interpreted as a photoinduced structural phase transformation. LIESST effects up to 105 K have now been reported.

A different class of spin isomers is provided by dioxolene-transition metal compounds [9–12]. Dioxolenes can be stable in the dinegative catecholate form, $Cat^{2-}$, in the mononegative semiquinonate form, $SQ^-$, and in the neutral quinone form, Q. In many cases it is indeed possible to assign a well-defined oxidation state to the dioxolene and to the metal ion. For instance cobalt can form two isomeric complexes $[Co^{III}(L)Cat]^+$ and $[Co^{II}(L)SQ]^+$ which interconvert and are called valence tautomers (here L is an ancillary ligand). While in spin cross-over systems the two isomeric species differ for the transfer of one electron between two metal orbitals, in valence tautomers an electron is transferred from a metal orbital to a ligand orbital or vice versa (Fig. 1).

On this respect, the process can be viewed as an intramolecular redox reaction involving the $Co^{III}/Co^{II}$ and the $Cat^{2-}/SQ^-$ couples. LIESST effect can be observed also in these systems, but in general the lifetime of the excited state is shorter than in spin cross-over systems. Recently relatively long relaxation times have been measured in cobalt derivatives [13].

As a general comment to this area, we want to stress the amazing variety of new experiments that can be performed in such an old field. There are exciting perspectives for applications, and perhaps more work should be performed in the investigation of single molecules, or at least of nanoaggregates. Detailed optical investigations, in particular using time-resolved techniques, Raman spectroscopy and Terahertz sources are also affording interesting results and, in the near future, can become a ripe field of physical research.

## 3. The quest for organic (molecular) ferromagnets

The original field that determined the start of molecular magnetism has not reached one of its main goals, namely the design of a room temperature organic ferromagnet. However, the demonstration that ferromagnetism can be realized through s and p electrons has been an important result and many important features, including the so-called Kagome lattices, were discovered. [14]. It has to be recalled that even the preparation of a room temperature molecular ferromagnet based on d-block elements has been an extremely challenging task. The Miller team broke the room temperature barrier with $V(TCNE)_x$ [15] and the Paris and Illinois groups came close by using Prussian blue derivatives [16].

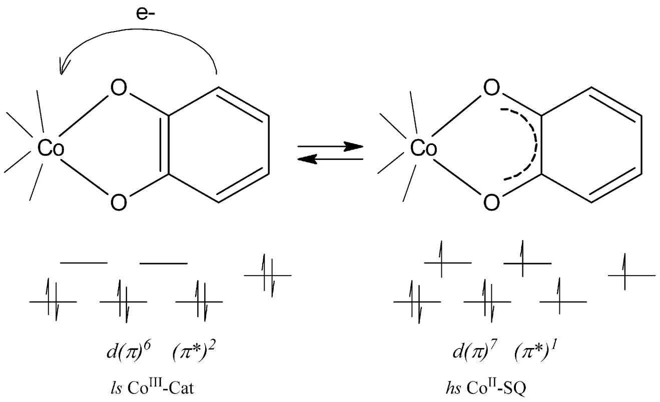

Fig. 1. Schematized view of the variation of electronic distribution occurring in valence tautomeric interconversion from low-spin Co(III)-catecholate, with no unpaired electrons, to high spin Co(II)-semiquinonato configuration, for which both ligand and metal are paramagnetic.