Molecular Magnets (MM)

An ESF scientific programme

The European Science Foundation acts as a catalyst for the development of science by bringing together leading scientists and funding agencies to debate, plan and implement pan-European initiatives.

F*or a long time,* Magnets *have found a wide range of applications in science, technology and domestic life. From audio or videotapes to door closures and car parts, they are present everywhere.* Molecular and macromolecular materials *are also encountered widely but in different areas such as plastics, woven synthetics, display technology, optics, etc. However,* molecular magnets *belong to a field which is still at an early stage of development. Research interest in this field is motivated by the need for a better understanding of the fundamental principles that govern magnetic behaviour, in particular when moving from isolated molecules to three-dimensional solids, as well as the need for new improved materials. The trend towards the miniaturisation of electronic devices to the ultimate scale – the molecular one – is a further force driving expansion of the field. While the biological world provides numerous examples which demonstrate that the route is feasible.*

The flexibility of molecular chemistry is particularly well suited to synthesising new magnetic systems in mild conditions (from solutions, at room temperature and pressure) and the first focus of the programme is to study how to synthesise new molecular magnetic systems with specific magnetic and electronic properties that might be suitable for future applications. The other principal focus is to provide the theoretical underpinning for designing such structures. The aim is to obtain a deeper understanding of how electronic and molecular structures (spin density, band structure, anisotropy, etc) relate to the macroscopic physical properties (magnetic, electrical, optical, etc).

This programme is therefore encouraging and stimulating the underlying research, trying in particular to respond to the great need for a much stronger fundamental science base to underpin the development of materials suitable for practical devices and useful applications in the future.

Introduction

A simple extrapolation of the decrease in the size of semiconductors and other components for electronic systems and computers leads to the prediction that molecular dimensions could be reached in a few years. To do this we need the ability to assemble molecular structures with given electronic and magnetic properties from the outside, using external signals such as photonic impulse, electric or magnetic field, or a temperature jump, to modify the state of the system. To reach this goal, several fundamental problems are still to be solved, such as details of the molecular driving forces, the nature of the co-operative interactions between the molecules, the properties of the molecule itself and the way to bridge the systems at a single-molecule level to the macroscopic world.

An important part of the overall research effort on molecular electronics involves a detailed study of molecular magnetism. This ESF programme is well placed to undertake this task, as it is exploiting research work being done in the relevant areas by established teams at the forefront of their fields. Some of them have made significant contributions in recent years, such as the discoveries of the first bimetallic molecule based magnets, organic magnets with the highest known Curie temperatures, molecular magnetic superconductors at ambient pressure amongst others.

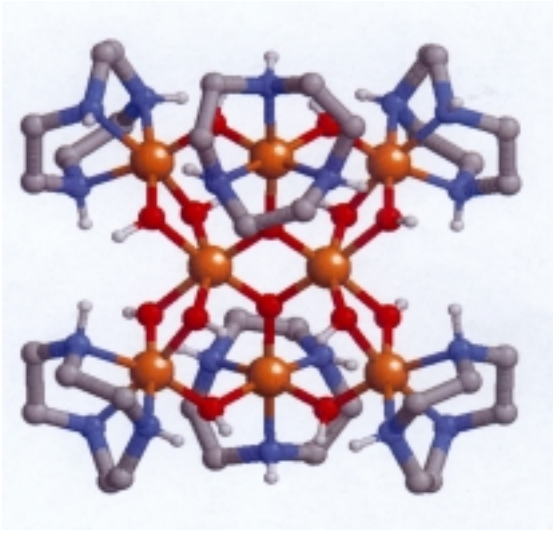
Scientific background

Research into molecular magnetism, and the closely related field of molecular electronics, is only some tens of years old, but is very active, with national programmes underway within most of the participating countries. It began in 1951 with the study of a dinuclear complex, copper acetate, but it received a strong impetus in the 1980s with the discovery of the first molecular-based solids that exhibited spontaneous magnetisation below their Curie temperature. A number of important discoveries have since been made by European teams in particular. These include:

- the synthesis of the first bimetallic molecular magnets and organic magnets with the highest Curie temperature known so far;
- the synthesis of room-temperature molecular-based magnets;
- the discovery of spin cross-overs that occur with large hysteresis at room temperature;
- new photomagnetic processes, including light-induced excited spin-state trapping;
- the synthesis of the first molecular-based magnetic superconductor;
- the first characterisation of magnetic tunneling effect.

There have also been many vital instrumental achievements without which the other research would not have been possible. Examples include:

- photomagnetic setups with multi-mode lasers;
- magnetic and heat capacity measurements at very low temperature ranges;



Fe_8: a single molecule magnet, with a spin = 10 ground state. © D. Gatteschi, Florence

Thanks to the molecular anistropy, the magnetic moments relax very slowly at low temperature and the systems behaves as a magnet without the need of interaction between neighbouring molecules. A phenomenon unknown five years ago.

- ability to determine spin distribution from polarised neutron diffraction data.

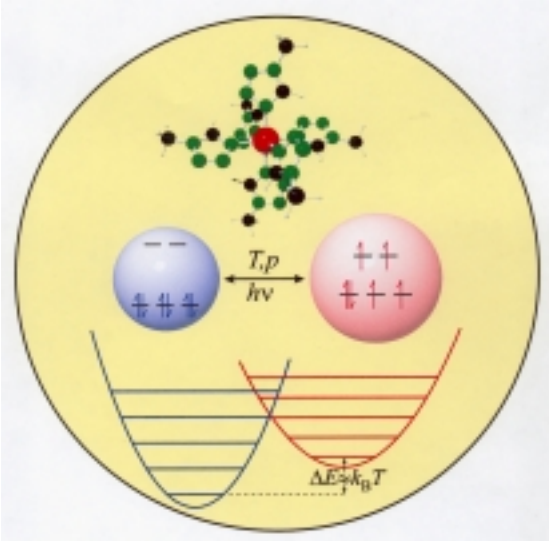
As has often happened before, the first technical applications have to some extent predated the science, in that for example liquid crystal displays came before any significant research in the field. But without a sound scientific framework such breakthroughs will continue to be few and far between, leaving the huge potential of the field largely untapped. Research is needed to make it possible to fabricate giant molecular assemblies in a controlled fashion with the ability to modify the structure and tune its properties at will via externally applied techniques, such as irradiation.

One of the great attractions of the whole field is the potential to build compounds that behave as classical solid state magnets while exhibiting completely new properties, such as a wide range of magnetic ordering temperatures, so that the relationship between magnetism and temperature can be precisely controlled.

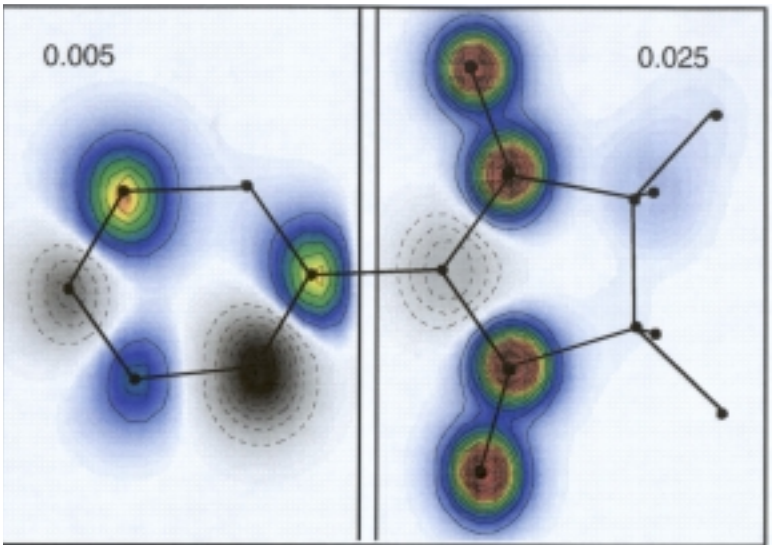
Before practical applications become possible however, there is significant theoretical as well as practical work to be done. On the practical side there needs to be further progress with instrumentation and the ability to control the fabrication process. On the latter front, both organic and inorganic precursors need to be examined. Organic materials have obvious potential as starting points since some of them have already been used by living organisms to fabricate molecular assemblies with desired magnetic properties.

On the theoretical side, there are several angles that need to be explored. One concerns the interaction between spin carriers. Several properties are relevant here: overlap and orthogonality, spin delocalisation, spin polarisation effects, which seem to play a crucial role in organic magnetism and vibronic effects, which are probably relevant in cases involving mobile electrons.

There is also work to do on the analytical/computational side, at various levels of sophistication: from semi-empirical valence electrons to *ab initio* all electron computations. Since analysing even relatively small assemblies of molecules in real time and space involves a large amount of computing power, Monte Carlo methods, in which the overall properties of a molecular cluster are analysed by considering just a sample of them, can be used.



Spin cross-over in Fe(II) complexes, example of bistability of molecular magnetic systems. © P. Gütlich, Mainz



Spin density in an organic magnet from spin-polarised neutrons diffraction.
© E. Ressouche, Grenoble

Aims and objectives

One of the ultimate dreams is to usher in a new era of electronics involving phenomena at the molecular level, bringing the benefits both of smaller component size, and materials with a whole new range of properties that can be readily tuned. But before the benefits can be obtained a lot of research needs to be done, and the programme aims to achieve progress in the following areas:

1● Assembly of giant molecular structures whose geometry can be modified as desired using an external structure. This is a difficult problem, but the programme hopes to make progress by examining new molecular architectures based on open-shell units using both organic and inorganic precursors.

2● New molecular magnets with tunable Curie temperatures and/or tunable coercive fields. The Curie temperature determines the temperature range in which the material can be used, while the coercivity gives the system a memory effect, *i.e.* with potential for semiconductors. Many synthetic approaches will be used, including the bimetallic one consisting of two magnetic metal ions assembled in controlled manner within the lattice, and the metal-organic approach using both metal ions and organic radicals (i.e. with unpaired electrons in C, N, O or p-type orbitals). All-organic materials will also be tried.

3● New bistable molecular systems, where the electronic spin can change direction under the influence of light, thermal energy or pressure, with obvious potential for future molecular electronic switching or display devices.

4● New multi-property materials, in which the magnetic property is combined with some other physical property. Examples include photomagnetic materials in which magnetism is modified by light irradiation; conducting and superconducting materials; and bistable materials which have stable long range magnetic properties coupled with a local instability where magnetic properties change abruptly.

5● New mesoscopic materials, filling the gap between quantum and classical systems. This includes single molecules that act as magnets, but also exhibit physical properties derived from the small scales and anisotropy of the system, such as bistability and quantum tunneling.

6● New molecules with multiple redox sites for testing long range charge and spin delocalisation in mixed valence compounds generated from the corresponding homovalent compounds presenting magnetic interaction.

7● New photo-induced magnetic and conducting behaviours.

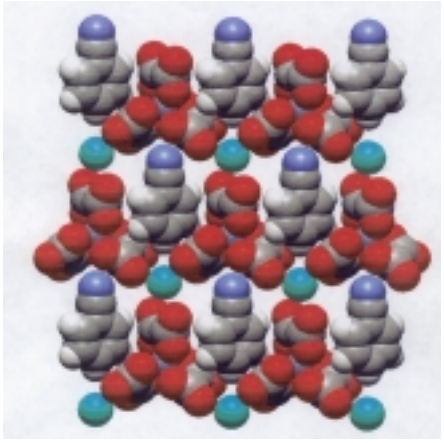
The ESF programme

The immediate objectives of the ESF programme can be categorised under two headings. One is the rational, or controlled, synthesis of new molecular systems that have specified magnetic and electronic multifunctional properties, such as bistability, and particular values for conductivity and optics. Research here will focus on how to control the interaction between the molecules in order to obtain the desired properties, and how to mimic existing biological mineral systems, such as ferritin (the protein that stores iron in the liver), which have properties operating at the molecular level to obtain a desired effect.

The second axis of development being followed by the programme is the endeavour to gain a deeper understanding of how the electronic properties of molecular systems relate to their physical characteristics, such as spin density, spin localisation and magnetic photo-excited states.

The programme builds on earlier national or European initiatives, establishing closer contact between experimentalists, theoreticians, chemists and physicists, at the time when achievements in these individual fields have reached a suitable point for exploitation in molecular magnetics.

In particular the programme is building on and enhancing existing multilateral collaborative programmes involving support from more than one member government. The programme is accelerating exchange of experiences and ideas between these existing initiatives, and significantly increasing overall European scientific activity in the field.



Anion layer in superconducting (C2/c) structures
© P. Day, London

In operational terms, the programme includes short individual visits of senior scientists and team leaders for seminars and exchanges, along with short fellowships for young researchers to improve their skills in a particular field. This training aspect is particularly important to help produce individuals with the required multi-disciplinary skills: training workshops on techniques, synthesis or theory are organised.

Then to coordinate the work and disseminate results there will be specialised meetings during the programme, culminating in two large European conferences before 2002.

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Molecular Magnets Steering Committee

Professor Michel Verdaguer (Chairman)
Laboratoire de Chimie Inorganique et Matériaux Moléculaires
Unité C.N.R.S. 7071
Case 42, Bâtiment F74
Université Pierre et Marie Curie
4 place Jussieu
75252 Paris Cedex 05
France
Tel: +33 1 44 27 55 62
Fax: +33 1 44 27 38 41
E-mail: miv@ccr.jussieu.fr

Professor Arnout Ceulemans
Quantum Chemistry Division
Department of Chemistry
Katholieke Universiteit Leuven
Celestijnenlaan 200 F
3001 Leuven
Belgium
Tel: +32 16 32 73 63
Fax: +32 16 32 79 92
E-mail:
Arnout.Ceulemans@chem.kuleuven.ac.be

Professor Peter Day
The Royal Institution
Davy Faraday Research Laboratory
21 Albermale Street
London W1X 4BS
United Kingdom
Tel: +44 171 493 2710
Fax: +44 171 499 2679
E-mail: pday@ri.ac.uk

Professor Silvio Decurtins
Anorganisch-chemisches Institut
Universität Zurich
Winterthurerstrasse 190
8057 Zurich
Switzerland
Tel: +41 1 257 46 51
Fax: +41 1 363 86 11
E-mail: silviozh@aci.unizh.ch

Professor Dante Gatteschi
Department of Chemistry
University of Florence
Via Magliano 77
50144 Florence
Italy
Tel: +39 055 362551
Fax: +39 055 354845
E-mail: gattesch@chim1.unifi.it

Professor Philipp Gütlich
Johannes Gutenberg-Universität
Institut für Anorganische Chemie und Analytische Chemie
Staundingerweg 9
55099 Mainz
Germany
Tel: +49 613139-2373 or 3221
Fax: +49 6131 39 2990
E-mail: p.guetlich@uni-mainz.de

Professor Olivier Kahn
Laboratoire des Sciences Moléculaires
Institut de Chimie de la Matière Condensée de Bordeaux
UPR 9048
Avenue du Dr. A. Schweitzer
33608 Pessac
France
Tel: +33 5 56 84 26 83
Fax: +33 5 56 84 26 49
E-mail: kahn@icmcb.u-bordeaux.fr

Professor Wolfgang Linert
Institute of Inorganic Chemistry
Vienna University of Technology
Getreidemarkt 9/153
1060 Wien
Austria
Tel: +43 1 58801 4639
Fax: +43 1 5816668
E-mail: wlinert@fbch.tuwien.ac.at

Professor Dragan Mihailovic
Institut Jozef Stefan
Jamova 39
1000 Ljubljana
Slovenia
Tel: +686 61 3729
Fax: +686 61 125 1077
E-mail: dragan.mihailovic@ijs.si

Professor Jerzy Mrozinski
Faculty of Chemistry
University of Wroclaw
14 F. Joliot-Curie
50-383 Wroclaw
Poland
Tel: +48 71 204 307
Fax: +48 71 204 420
E-mail: jmroz@chem.uni.wroc.pl

Professor Fernando Palacio
Instituto de Ciencia de Materiales de Aragon
CSIC
Universidad de Zaragoza
50009 Zaragoza
Spain
Tel: +34 976 76 1227
Fax: +34 976 76 1229
E-mail: palacio@posta.unizar.es

Professor Jan Reedijk
Leiden Institute of Chemistry
Gorlaeus Laboratory
Leiden University
P.O. Box 9502
2300 RA Leiden
The Netherlands
Tel: +31 71 527 44 59
Fax: +31 71 527 45 37
E-mail: reedijk@chem.leidenunivl.nl

Professor Hans Toftlund
Odense University
Chemistry Department
Campusvej 55
5320 Odense
Denmark
Tel: +45 6557 2543
Fax: +45 66 15 87 80
E-mail: hto@dou.dk

Dr. Svenje Mehlert
ESF Scientific Secretary

Mrs. Catherine Werner
ESF Administrator
European Science Foundation
1 quai Lezay-Marnésia
67080 Strasbourg Cedex
France
WWW Home Page:
http://www.esf.org
Tel: +33 (0)3 88 76 71 28
Fax: +33 (0)3 88 37 05 32
E-mail: cwerner@esf.org

For the latest information on this programme consult the *Molecular Magnets* home page:
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Cover picture:
Building crystals and molecules with given magnetic properties begins with the synthesis.
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