

# Molecular magnetism: mesoscopic and nanoscopic structures

D. Gatteschi

Department of Chemistry, University of Florence, INSTM

All the magnets currently used are based on metallic or ionic lattices. Since about two decades chemists have started a thorough project of using molecular chemistry techniques to develop new classes of magnets based on molecules rather than on metals or oxides. The idea behind this is the challenge of creating new classes of materials from which new exciting properties may be expected. In a sense this research is the continuation of that which was successfully developed when it was discovered that organic compounds can behave as conductors and superconductors like the classic inorganic materials. In a few years it has been discovered that purely organic magnets are indeed possible, although the critical temperatures are still very low. The most promising results have been obtained using sulfur-nitrogen based organic radicals which behave as weak ferromagnets below 35 K [1]. On the other hand, using a mixture of transition metal ions and organic radicals it has been possible to obtain a room temperature ferrimagnet [2], and similar results have been obtained using derivatives of the old Prussian Blue compounds [3].

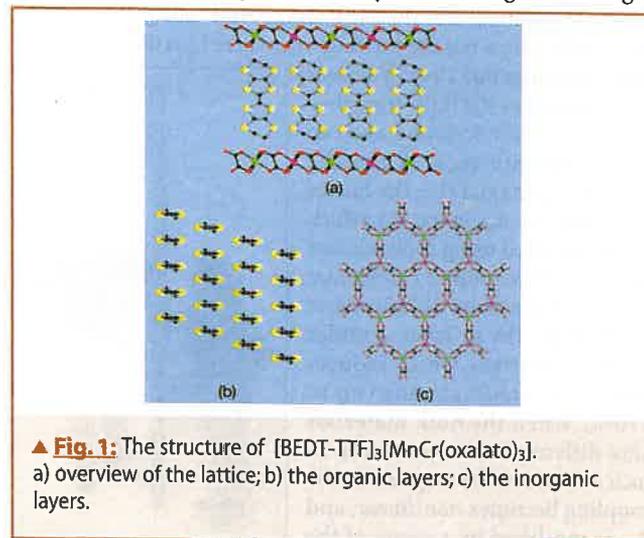
Beyond the chemical challenge of assembling new structures using moderately stable building blocks like organic radicals, the factors suggesting that molecular magnetism can indeed provide new interesting classes of materials are:

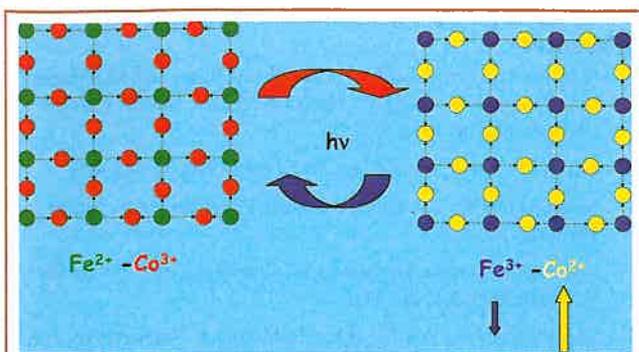
- The possibility of fine tuning the properties of the materials by using flexible molecular techniques
- The possibility of building a la carte magnetic molecules of increasing size which behave as molecular nanomagnets
- The possibility of obtaining multifunctional materials

An example of the last possibility has been recently reported by Coronado *et al.* [4] They used a hybrid approach, assembling together inorganic building blocks like transition metal oxalato

derivatives and organic radicals like the famous BEDT-TTF, well known to form conducting and superconducting materials. They obtained by electrocrystallisation a compound of general formula  $[\text{BEDT-TTF}]_3[\text{MnCr}(\text{oxalato})_3]$ . The structure comprises honeycomb inorganic layers of  $[\text{MnCr}(\text{oxalato})_3]^-$  separated by stacks of the organic radicals, as shown in Figure 1. The average charge on the BEDT-TTF molecules is +0.34. The inorganic layer is insulating while the organic moiety is a conductor. The magnetic coupling is fairly strong within the inorganic layers and this, coupled to the fact that weak interactions are operative between the layers determined a transition to bulk ferromagnetic behaviour below 5.5 K. Therefore below the critical temperature the material behaves as a ferromagnetic conductor. Although systems like this are well known starting from iron itself, in the molecular derivative the magnetic electrons are different from the conducting electrons, thus offering the possibility of observing new phenomena.

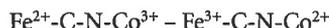
Another important feature of molecular magnets is that they are in general insulators, therefore they are much more transparent to UV—visible light than classic magnets. Therefore it is possible to use light to induce magnetic transitions. This approach has been used by the groups of Verdaguer and Hashimoto for instance.[5,6] Prussian blue derivatives are complex cyanides of general formula  $\text{ABC}(\text{CN})$ . When  $\text{B} = \text{Fe}^{2+}$  and  $\text{C} = \text{Co}^{3+}$  the compound is diamagnetic because both ions are in their low spin, non-magnetic state. By illuminating with red light





▲ Fig. 2: Scheme of the light induced interconversion of Prussian blue derivatives.

however it is possible to induce an electron transfer in which  $\text{Fe}^{2+}$  is changed to low spin  $\text{Fe}^{3+}$ , with one unpaired electron, and  $\text{Co}^{3+}$  to high spin  $\text{Co}^{2+}$  with three unpaired electrons:

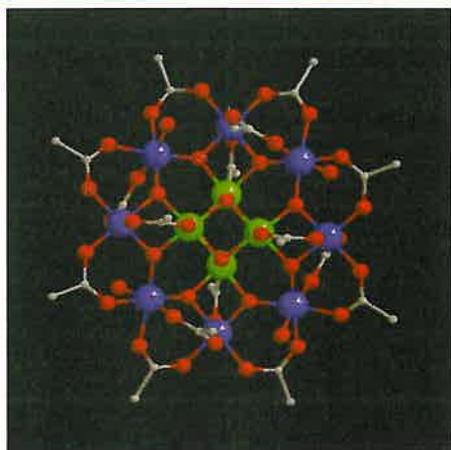


A schematic drawing of the light induced transformation is shown in Figure 2. The material orders as a bulk ferrimagnet below 50 K. If the irradiation is performed below this temperature we observe a transition to bulk magnetic order induced by light. Therefore these materials can be considered as magnetic switches operated by light. It is also possible to perform the opposite transition by irradiating the  $\text{Fe}^{3+}\text{-Co}^{2+}$  pairs with blue light: the electron is back transferred from cobalt to iron and the system reverts to the diamagnetic state.

The most exciting developments of molecular magnetism of the last few years has been the discovery that some discrete molecules can behave at low temperature as tiny magnets. [7] The archetypal molecule is:



Mn12Ac for short. The structure of the dodecanuclear manganese cluster is shown in Figure 3. It comprises an external ring of eight manganese(III) ions and a tetrahedron of manganese(IV) ions, bridged by oxide bridges, like in a manganite. Acetic acid molecules complete the environment of the metal ions, in fact blocking the growth of the oxide particles. In other terms these clusters can



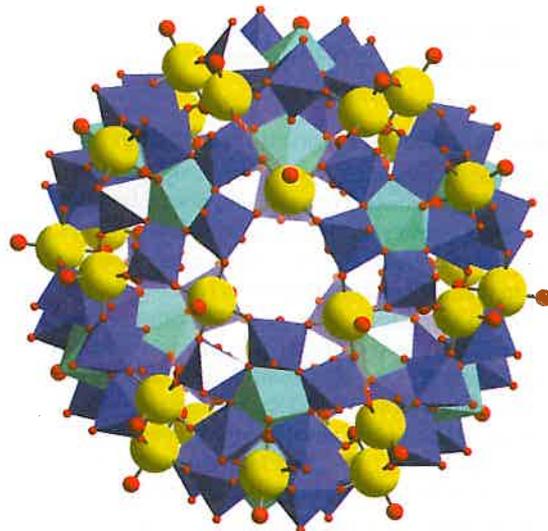
▲ Fig. 3: Sketch of the structure of Mn12Ac.

be considered as small particles of manganese oxides, all identical to each other. In this particular case the particles crystallise in a tetragonal space group, and therefore they are also iso-oriented in the lattice. At low temperature the system is in the ground  $S=10$  state, with the eight  $S=2$  spins of manganese(III) up and the four  $S=3/2$  of the manganese(IV) ions down. The clusters have a high Ising type magnetic anisotropy, due to the local anisotropies of the distorted manganese(III) ions. This means that the magnetisation is preferentially oriented parallel to the tetragonal axis of the cluster and to reorient itself it needs a high activation energy. At 2 K the relaxation time of the magnetisation becomes so long that the individual molecules become permanently magnetised, like tiny magnets. They show magnetic hysteresis and in principle information can be stored in one molecule, thus reaching the highest possible level of miniaturisation. But the excitement does not stop here, because Mn12Ac shows a rich range of quantum properties, and it has been proved to be an ideal test ground for theories of quantum effects in magnets. Clear evidence of tunnelling of the magnetisation has been achieved by observing stepped hysteresis. More controversial still is the possibility to observe quantum coherence.

The advantage of magnetic molecules over other types of magnetic particles is that they are absolutely monodisperse, and that in principle they can be diluted and organised using supramolecular chemistry techniques. Many efforts are currently made to derivatise the magnetic molecules to organise them on suitable supports, like gold or silicon, in order to be able to address them individually. The dream of storing information in one molecule may become reality!

After Mn12 a few other types of single molecule magnets have been discovered and investigated. Among these a cluster containing eight iron(III) ions has been found to show oscillations of the tunnel splitting in the presence of an applied transverse magnetic field. This is the signature of the Berry phase in magnets which was first reported by Sessoli and Wernsdorfer in 1999. [8]

Recently it has been discovered that similar effects of slow relaxation can be observed in one-dimensional magnets. [9] A compound containing  $\text{Co}^{2+}$  ions regularly alternating in space with organic radicals behaves as a one dimensional ferrimagnet. Below 20 K the relaxation time of the magnetisation rapidly



▲ Fig. 4: The structure of  $[\text{Mo}_{75}\text{Fe}_{30}]$  clusters. The yellow circles are iron(III) ions.

increases on decreasing temperature, with a barrier for the re-orientation of the magnetisation larger than 150 K. Also in this case magnetic hysteresis is observed which is associated with a high magnetic anisotropy of the easy-axis type. A semi quantitative explanation has been provided using a model proposed by Glauber in 1963. This opens an exciting perspective, that of allowing the storing of information in segments of a polymer, which therefore behaves like a magnetic nanowire.

Finally I want to mention that magnetic molecules are also interesting in the case of antiferromagnetic behaviour. Perhaps the most significant example is that of a cluster [10] containing 76 Mo<sup>6+</sup> ions and 30 Fe<sup>3+</sup>, which has the structure shown in Figure 4. The molybdenum ions are non-magnetic so the magnetic behaviour is associated with the interactions between the iron ions. They are antiferromagnetic, and highly frustrated due to the particular topology which corresponds to an icosidodecahedron. The compound has not shown quantum effects down to the mK region, due to the large degeneracy of the low lying states associated with spin frustration.

Molecular magnets open many new possibilities to observe quantum and classic effects in mesoscopic matter. The field is just at its beginning, but many developments can be anticipated in the next few years. Possible applications may range from quantum computing to new types of contrast agents for magnetic resonance imaging.

## References

- [1] Banister, A. J.; Bricklebank, N.; Lavender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew Chem Int Ed Engl* **1996**, *35*, 2533
- [2] Müller, J. S. E. A. J. *Angew Chem Int Ed Engl* **1994**, *33*, 385-415.
- [3] Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701-703.
- [4] Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447-449.
- [5] Sato, O.; Iyoda, A.; Fujishima, K.; Hashimoto, K. *Science* **1996**, *272*, 704.
- [6] Verdaguer, M.; Bleuzen, A.; Marvaud, V.; Vaissermann, J.; Seuleman, M.; Desplanches, C.; Scullier, A.; Train, C.; Garde, R.; Gelly, G.; Lomenech, C.; Rosenman, I. V. P.; Cartier, C.; Villain, F. *Coord. Chem. Rev.* **1999**, *190-192*, 1023-1047
- [7] Gatteschi, D.; Sessoli, R. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 268-297. Friedman, J. R Sarachik, M.P. Tejada J. Ziolo R., *Phys. Rev. Lett.* **1996**, *76*, 3830 ; Thomas, L. ; Lioni, F. Ballou, R. Gatteschi, D. Sessoli R. Barbara B., *Nature* **1996**, *383*, 145.
- [8] Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133-135.
- [9] Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. "Cobalt(II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires" *Angew. Chem. Int. Ed.*, **2001**, *40*, 1760-1763.
- [10] Müller, A.; Luban, M.; Schröder, C.; Modler, R.; Kögerler, P.; Axenovich, M.; Schnack, J.; Canfield, P.; Bud'ko, S.; Harrison, N. *Chemphyschem* **2001**, *2*, 517-+.