PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Perspective

The emergence of complex behaviours in molecular magnetic materials.

Karin Goß,[a] Dante Gatteschi[b] and Lapo Bogani*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Molecular magnetism is considered an area where magnetic phenomena that are usually difficult to demonstrate can emerge with particular clarity. Over the years, however, less understandable systems have appeared in the literature of molecular magnetic materials, in some cases showing features that hint at the spontaneous emergence of global structures out of local interactions. This ingredient is typical of a wider class of problems, called complex behaviours, where the theory of complexity is currently being developed. In this perspective we wish to focus our attention on these systems and the underlying problematic that they highlight. We particularly highlight the emergence of the signatures of complexity in several molecular magnetic systems, which may provide unexplored opportunities for physical and chemical investigations.

1. Introduction

The traditional approach of physical and chemical sciences to a problem is to first find a model system, where a certain effect can be isolated and studied clearly. The understanding thus achieved is then used to solve more thorny situations. When multiple effects are present, the problem will be cut down into its components, and treated as a sum of interacting systems. Nevertheless, there is compelling evidence that not all systems can be treated using this approach: there are so-called "complex" systems, which cannot be worked out this way.[1] Such complex behaviour are situated between order and disorder: they are neither predictably regular, nor completely random and chaotic, lying somewhere in between.[2] Complex behaviours appear in seemingly-unrelated areas of very considerable importance, such as transport and social interactions,[3] the behaviour of markets[4] and the evolution of organisms (Figure 1a).[5] Although such areas might seem completely unrelated, a common background is now emerging that can explain the features of many such behaviours. In materials science, complexity is a constant presence in highly-correlated systems,[6] and has been considered an important component of colossal magneto-resistance effects[7] and of several high-temperature superconductors.[8]

Molecular magnets[9] (MMs) have arisen to some prominence, in the material science community, mainly because some of their examples provide very clean testgrounds for quantum effects, where unwanted contributions can be minimized. On the other hand, now that many properties of single magnetic molecules are understood, attention is gradually shifting to interacting systems. A reconsideration of the literature also shows that, alongside the better-known ultra-clean MMs, examples of complex magnetic behaviour may have appeared. Several features displayed hint at the spontaneous emergence of global structures out of local interactions, as typical of complexity. In these cases, a different perspective has to be adopted to treat the systems. Even crowds can be modelled to a good degree of accuracy, but only when taking into account the non-obvious patterns of interaction and influence among people that lead to complexity.[4] Similarly, complex spin systems cannot be understood by a correction to the usual magnetic models, and in this perspective we wish to

Karin Goß obtained her PhD at the Research Center Jülich, Germany, on transport and spectroscopy of carbon nanotubes, for which she received the 2011 "Best PhD Dissertation Award" from Universität Duisburg-Essen. She is now performing research in Stuttgart, Germany, on molecular and carbon nanoelectronics.

Dante Gatteschi is professor of chemistry at the University of Florence, Italy. He is member of the Leopoldine, XL, European and Lincei academies. His work in molecular magnetism and EPR count more than 600 publications. He has been awarded, among other awards, the Nasini, Agilent and Brüker-EPR prizes.

Lapo Bogani, after a PhD in Florence (IT) and an individual Marie Curie fellowship, is now ERC and Sofja Kovalewskaja group leader in Stuttgart, Germany. His work on single nanomagnets, and functional nanostructures has led to several awards, including the G. Semerano, R. Nasini, Burghen and N. Kurti prizes.

provide a perspective on such systems, highlighting past observations of complexity in MM and showing how complexity will likely become more and more relevant in the future. Here we consider three main reasons for the appearance of complex behaviour in MMs: structural sources are investigated first, as they are more intuitive and point at synthetic strategies; the second source is the interaction pattern among the magnetic centres in the compound, and we particularly consider the most simple systems, those with one-dimensional structure; the third source is, eventually, the interaction with external baths, such as electrons and phonons. A unifying perspective, bridging several emerging areas such as slow-relaxing molecular spin chains, molecular magnets on surfaces and molecular spintronics, can then emerge.

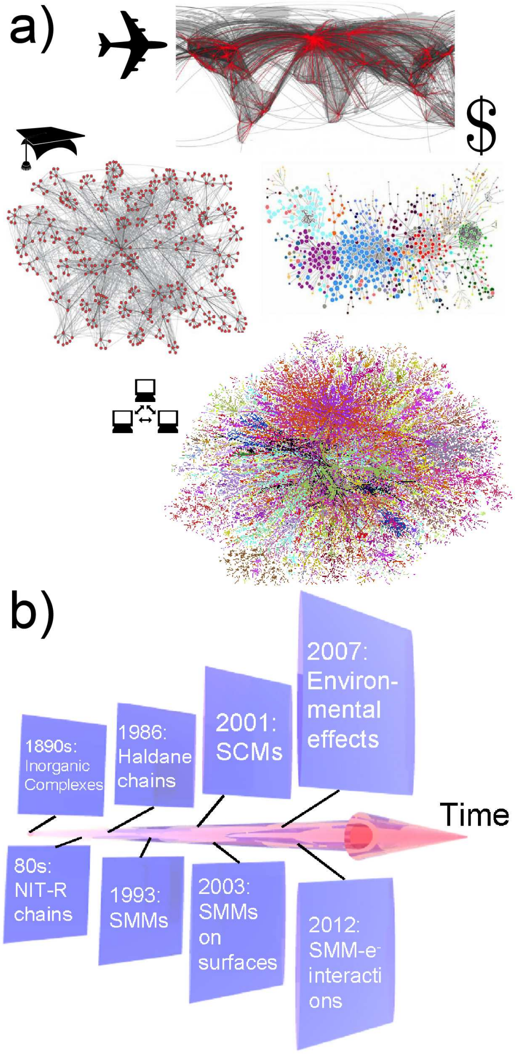
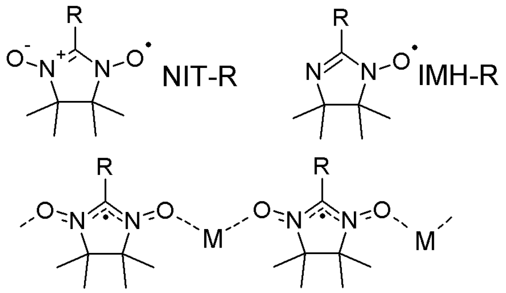


Fig.1 a) interaction networks created by some complex systems, including, on proceeding clockwise: the worldwide aviation transport system;[3d] the economic exchanges of Japan;[4d] the internet in 2001;[3b] the scientific collaborations of mathematicians.[3c] b) Timeline of some key developments in molecular magnetism, with particular focus on complex behaviour and phases relevant to single-molecule investigations.

The relationship between magnetic systems and complex behaviour has been longstanding and fruitful. Probably, the best-known and studied examples are spin-glasses,[10] where theoretical models have then been applied to the understanding of other complex phenomena, most notably neural networks.[11] Contrarily to these systems, MMs can be being integrated into hybrid systems or organized into functional nanostructures, where complexity can emerge from the interaction with the many degrees of freedom of the environment.[12] In this sense, MMs may be one of the first instances where materials made with a bottom-up approach find application in the study of complexity, and they might actually be particularly well suited for such studies.[12,13]

2. Structural sources of magnetic complexity

Complex systems often include very structured, non-regular interaction patterns[3-8,10-13] (e.g. the social interaction patterns among humans,[3] or the node patterns of neural networks,[11] see Fig. 1a) and some form of disorder, which can either be structural and intrinsic to the system, or may arise from random fluctuations (e.g. in economics). In this paragraph we discuss some of the chemical possibilities that lead to complex behaviour from structural sources in MMs. We start by considering 1D complex systems, as they are often the starting point to understand systems with higher dimensionality. In magnetic chains, complex behaviour can arise from the internal interactions, as famously shown by Haldane, who first suggested that 1D antiferromagnets with integer spins can have exotic, disordered ground states.[14] Although, as we will show in the following, 1D MMs often show complex characteristics due to other causes, it was indeed in MMs that such predictions could be confirmed.[15] Additionally, molecular quasi-1D magnetic structures (Scheme 1) have inter- and intra-chain interactions, which can be tuned to create complex behaviour. The most common source of complexity, on the other hand, arises from disorder which strongly affects 1D systems: as there is only one channel to transmit the magnetic interaction, defective sites alter the spin correlation in the whole system, strongly affecting the overall behaviour.



Scheme. 1 (top) Structure of nitronyl-nitroxide (NIT-R) and imino-nitroxide (IMH-R) radicals (one of the resonant forms). The R substituent can be varied at will. (bottom) Coordination producing magnetic polymers, with M a neutral metal complex.

Nitronyl-nitroxides (NIT-R, scheme 1) offer a particularly interesting case of complexity arising from structural disorder and correlations, which still poses open questions. NIT-Rs are versatile organic radicals that coordinate to transition-metal and lanthanide ions in a variety of fashions.[16] In 1D materials the oxygens bind to two different metal ions (Scheme1). When carboxylates are used to bind Mn(II) centres, a structure of chains interlocked by hydrogen bonds develops.[17] Disorder is introduced by the fact that half of the NIT radicals are reduced to the imidazoline form IMH,[17] and the Mn ions bind to four radicals, either in the NIT or IMH form. The hydrogen bond network imposes that, if there is a NIT radical in one site of a chain, the proximal site of the neighbouring chain must be an IMH radical (Figure 2). Ordered structures of molecular organization become possible, only if there is a relation between neighbouring sites inside the same chain (Figure 2a,b,c). When chain atoms impose no constrain on their intrachain neighbours, as indeed the case in the experimental systems (Figure 2d), the result is an overall disordered structure with emergent correlations. This is nicely displayed by the dispersion of possible configurations: assuming independent chains the number of possible configurations of the NIT and IMH on a chain of M sites is given by: $n_1 = M!(M!/2)^{-2}$ and N independent chains have $(n_1)^N$ configurations; with the NIT in one chain forcing the presence of a IMH in the neighbouring one, we have:

$$n_N = M!\left(\frac{M}{2}!\right)^{-2}\left[\frac{(M/2)!}{(M/4)!}\right]^{N-1} \approx \left[\frac{(M/2)!}{(M/4)!}\right]^{N} \qquad (1)$$

which lies between a completely ordered situation and a disordered one. This complex crystalline features are also transmitted to the magnetic properties, which, at the moment, cannot be reproduced with known models, and are currently under study using the tools derived by the study of complex systems. These compounds thus constitute a beautiful example of how complex behaviour may emerge from structural features.

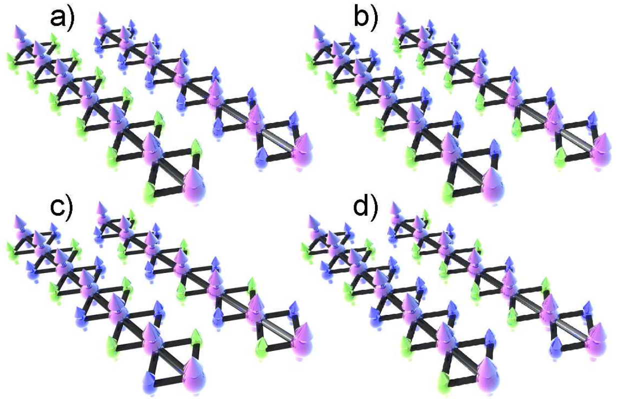


Fig.2 Structural and magnetic models for chains of [Mn($CH_3COO)_2$NIT-Me].[17] Arrows represent spin centers: pink is Mn(II), blue is NIT-Me and green is IMH-Me. All panels include constraints on neighbouring chains, so that a NIT-Me always imposes a IMH-Me in the corresponding position of the neighbouring chains. Panels a, b, c also include intrachain relations between radicals, while d releases all intrachain constraints. a) One chain is fully M-NIT, the neighboring ones are M-IMH; b) Regular alternation of NIT and IMH on the same chain; c) double alternation, disordered only if different planes have random orientation; d) completely disordered situation, as experimentally apparent.

Structural effects have also emerged as fundamental for the magnetization dynamics of molecular chains. Slow relaxation of the magnetization and hysteresis can appear in certain 1D systems,[18] called single chain magnets (SCMs hereafter).[19,20] SCM behaviour follows Glauber's model for Ising chains[21] (Fig.3) but, owing to the presence of defects, SCMs should rather be viewed as a collection of independent segments of different lengths L.[22] Defective sites thus geometrically limit the spin correlation length ξ. Two dynamical regimes can then be identified:[23] when the average chain length $\overline{L}$ is longer than ξ, the dynamics starts by a spin flip at the expense of overcoming the exchange interaction with two neighbouring spins, for a total energy cost of 4 times the coupling J. The relaxation time τ diverges exponentially as $\tau = \tau_0 \exp(4J/k_B T)$, where τ_0 is the inverse of the spin-flip rate at the border between two domains.[20,21] When $\overline{L} \ll \xi$ the dynamics is dominated by spin flips at the chain ends, costing $2J$. Statistical arguments[23] show that the relaxation time τ_L of a segment of L spins now depends on the segment length as $\tau_L = L\tau_0 \exp(2J/k_B T)$.

These interesting dynamics very quickly enter the domain of complex systems as soon as interchain magnetic shielding is not very efficient. The contemporary presence of random defects and interchain interactions (often competing with intrachain ones) leads to a behaviour which is reminiscent of spin-glass-like (SGL) systems.[10] SGL are undoubtedly good examples of complexity arising from two ingredients: disorder and competing interactions.[10] The first can be produced by structural disorder (random defects, random placement of the spins, etc...) or other physical parameters (randomly-oriented magnetic axes, random size, etc...). Competitive interactions will then act differently on these random units, leading to a multitude of energetically-equivalent states, often separated by large barriers, which make relaxation to the true ground state extremely slow.[10] The material can also respond following a number of different paths, when subject to a stimulus. Below a certain T the labyrinth of possible configurations is so intricate that the system will get stuck into a disordered, frozen state of the magnetization without 3D order.[10] A distribution of relaxation times $G(\tau)$ is to be expected,[10] due to the simultaneous presence of randomness and frustration. $G(\tau)$, from being roughly gaussian and narrow, broadens on lowering T,[22] as interactions vary with the degree of magnetic freezing. Impurities and defects that break SCMs into *non-interacting* segments also give rise to a distribution of relaxation times $G(\tau)$. On the other hand, such a distribution is not a necessary ingredient of the slow dynamics[10] and its shape depends only on the geometrical length of the chains. Consequently, the Arrhenius law meaningfully describes a microscopic mechanism and

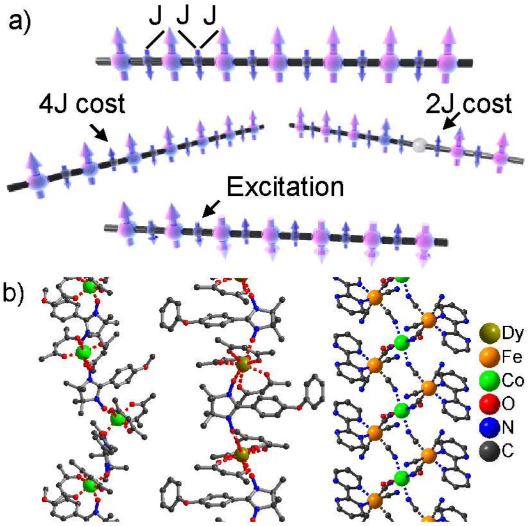


Fig.3 a) Relaxation mechanism of a ferrimagnetic SCM, with the starting configuration (top), the nucleation of the magnetic excitation within the chain or at a defective site (middle) and the propagation of the excitation (bottom). b) Crystal Structures of the $[Co(hfac)_2NIT(Me\text{-}O\text{-}C_6H_4)]_\infty$ and $[Dy(hfac)_3NIT(Ph\text{-}O\text{-}C_6H_4)]_\infty$ SCMs, as well as the cyanide-bridged heterometallic $[(Fe(bpy)(CN)_4)_2Co(H_2O)_2]_\infty$, which shows complex dynamics. Hydrogen and fluorine atoms omitted.

reflects the shift of the whole $G(\tau)$. In SGL systems, on the contrary, the Arrhenius law has no direct physical meaning, as there is simply a $G(\tau)$ that spreads and becomes distorted on lowering the temperature.[10] One of the current challenges is to be able to follow precisely the temperature dependence of $G(\tau)$ for SCMs with interplay to SGL dynamics.[23] This would provide the necessary information to understand the dynamical region between SGL systems and SCMs. Theory predicts that the passage between the ergodic and non-ergodic magnetic phases that is found in this intermediate region will display particularly interesting features of complexity,[24] where otherwise-unstable spin configurations can become dynamically accessible owing to the slow relaxation of SCMs that sets in before the SGL freezing. MMs, allow the fine tuning the ratio between intra- and inter-chain couplings by creating compounds with slight structural variations, and appear particularly promising for such investigations.

3. Complex magnetic phases in low dimensions

The symptoms of complexity can also arise, in low dimensional MMs, due to intricate interaction patterns. These properties often arise because the exchange interactions between spins in the chain are not limited to nearest neighbours (NNs). In this way the magnetic material can reproduce, topologically, many of the features that are typically associated with higher-dimensional systems or with intricate networks. Here we wish to highlight how molecular chains have allowed observing ling-predicted complex phases, from carefully-tuned NN and next-nearest-neighbour (NNN) interactions only. Several rare-earths possess helical magnetic structures due to competing exchange interactions.[25] In these cases chirality is accompanied by the contemporary creation of a well-defined helical pitch. But is chirality always found with helicity, or are intermediate phases possible? And how does the transition from paramagnetic to helical phase happen?

Gd(III) has very low magnetic anisotropy, and, except for very special cases, it is of little use for slow-relaxing magnetic materials. However, combined with NIT-R radicals, it shows the presence of NN and NNN interactions of opposite sign and similar magnitude.[26] The simple up-down spin description must be abandoned and small perturbations can dramatically affect the resulting ground state.[27] In Villain's theory of purely chiral spin chains,[27] the presence of weak interchain interactions can thus stabilize magnetic states where the spins turn around the chain axis always in the same screw direction, but with no regular pitch. It can be conceived as the magnetic equivalent of a spiral staircase with the steps having different heights and widths, but still following the spiral. MMs offer very good samples to probe such effects with techniques that monitor different types of spin correlations. Muon spin resonance and magnetization experiments measure two-spin correlations, while specific heat measurements are also sensitive to four-spin correlations. The combination of different techniques has recently allowed observing such complex phases in MMs:[28] a high-T transition to chiral order and a low-T one to a complex, chiral phase[29] having rotational but no translational invariance were observed in molecular $[Gd(hfac)_3NIT\text{-}Et]_\infty$ chains (Fig.4).

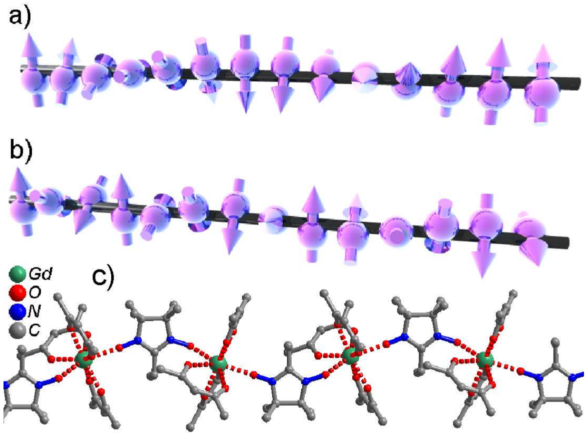


Fig.4 a) Helical spin order in a magnetic chain, with a regular, well-defined pitch. b) Chiral spin order, in which the spins always rotate in the same direction with no defined pitch. c) Structure of the $[Gd(hfac)_3NIT\text{-}Et]_\infty$ chain, where a purely chiral magnetic phase was detected. Hydrogen and fluorine atoms omitted for clarity.

Models of complex phases investigated in MM have found application in other systems with electronic delocalisation, such as mixed oxides. Competing NN and NNN have been observed in $LiCu_2O_2$, where Cu assumes two different and segregated valences, forming a two-legged triangular ladder,[29] and incommensurate antiferromagnetic order was evidenced by neutron diffraction. These results test long-unverified theories of how complex states arise from just the magnetic degrees of freedom. If we consider the effect of external interactions, as we explore in the next section, we will find an even deeper level of complexity, which plays a fundamental role for several emerging fields.

4. Complexity from external baths

Up to now we have considered spin systems isolated from their environment. Even for low-dimensional magnetic materials, this is not a safe assumption: spins feel a number of external influences, or baths, e.g. possible delocalised electrons, lattice vibrations, nuclear spins, etc. All these sources of interaction play a role in the final dynamic properties of the systems, and the importance of the phonon bath was already perceivable when we had to introduce the spin-flip rate in SCMs and SGL systems:[10,22] for the spin to attempt flipping, it must have the possibility to interact with an external bath and exchange angular momentum with it. The interaction with these external degrees of freedom is usually a complex one, even when considering ordered crystalline materials, because the baths often introduce multi-particle interactions. The effects on surfaces and in hybrid materials can be even more intricate and can lead to amazing effects. Research in this area has barely begun and here we will focus on the first results, at the same time trying to highlight some of the many still-open questions.

Most magnetization dynamics models consider a simplified lattice-spin interaction, assuming that only the difference between the initial and final spin states and the phonon density at that energy[30] matter for a spin. This is called the Metropolis argument[31] and is very widely accepted. On the other had, low-energy phonons have long wavelengths and will thus interact with a large number of spins at the same time. Additionally, if the spin-orbit interaction affects the spins, it will contemporarily affect the vibrational modes. The importance of such effects suddenly became clear with the BCS theory of superconductivity,[32] and strong phononic interactions play an important role in the notoriously complex high-T superconductors[33] and spin-Peierls systems.[34] SCMs offer an excellent opportunity to test the effect of correlation on the spin-phonon interactions. The possibility of comparing monomers and chain systems[24] and investigating them with unprecedented clarity is particularly appealing.

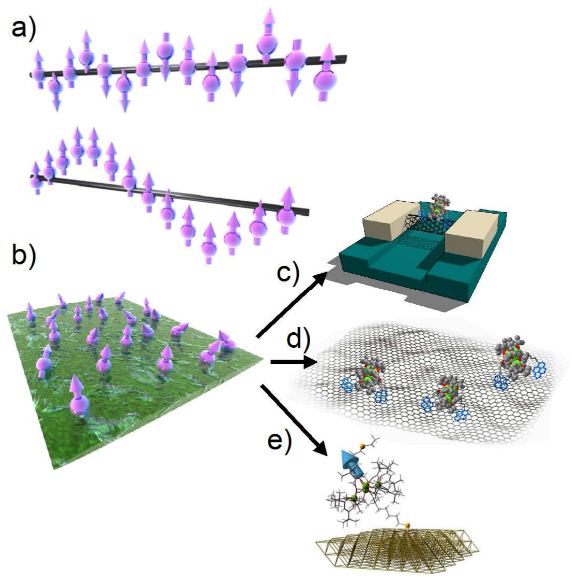


Fig.5 a) Schematic representation of phonon-spin correlation effects where the phonon wavelength (exaggerated vertical spin displacement) changes for short (top) and long (bottom) spin correlation lengths. The role of transverse phonons is omitted for clarity. b) Molecular spins interacting with a Fermi-sea of delocalised electrons, which can lead to complex interactions and phenomena. Experimental realizations in reduced dimensions using SMMs of the Fe$_4$ family include: b) SMMs on CNTs; c) SMMs on Graphene; d) SMMs on metallic surfaces.

The role of the spin environment, on the other hand, is not only restricted to the vibrational bath. The possibility that the dynamics of spin systems can be strongly altered by environmental effects was first shown using magneto-optical techniques on crystals, SMMs included in resins, Langmuir-Blodgett films and assembled on surfaces[35] and, more recently, by studying SMMs assembled on graphene.[36] The general trend is that the dynamics becomes progressively faster on proceeding further away from the ordered crystalline form.[35] For systems where the phononic bath can be modelled, such as graphene, the introduction of the novel phononic densities provides excellent reproduction of the magnetization dynamics. On the other hand, he origin of this complex effect is still not clear: and can be linked to distortions around the molecules, or modified molecular rotations.[37]

The interaction with charge carriers is fundamentally important when organizing SMMs on surfaces, which needs novel experimental tools. Some are being developed in the raising field of molecular spintronics,[38] which relies on the mutual influences between conducting and MM systems. The first steps will come from the study of hybrid carbon structures[39] (Fig.5), where SMMs can interact with a well-defined electronic gas whose dimensionality can be tuned by using carbon nanotubes[40] (CNTs) or graphene.[41] Knowledge of the symmetry of the conducting system is here a huge advantage, as it allows identifying interaction effects via symmetry considerations.

As the interplay between SMMs and the electron gas is mutual, we can expect variations not only in the magnetic behaviour but also in the electronic one. This can lead to spintronic devices,[42] where complexity has long played an important role and the importance of chemical aspects[43] and many-body phenomena can hardly be underestimated. Kondo physics[44] and the screening of magnetic impurities by the electronic states have already been observed on single magnetic molecules.[45] In these experiments full admixing of the conductor and molecule wavefunctions is attained, and the resulting behaviour offers all ingredients of complexity. The expansion of MM in this area will allow better control over the interaction with the delocalised states and fine tuning of the hybrid systems.

5. Conclusions

Are phases between order and disorder really stable? What is the effect of self-organization on the magnetic properties of molecules? What happens when magnetic molecules interact with complex external baths? The last steps in molecular magnetism now lead towards single molecule addressing, which may seem the final frontier of simplicity. But what happens when environmental effects start playing a huge role, and our individual molecules are no longer in the "safe" environment of the crystal phase? All these questions are key points for the development of molecular magnetic nanodevices, and are playing an increasingly important role in molecular magnetism. They all share a common point: to answer them the focus has to be shifted from the properties of single, well-defined systems to the collective behaviour of disordered structures, with multiple interaction patterns and mechanisms. These features can make molecular magnetic materials much closer to very different classes of systems, called complex, where the models to be used to understand the behaviour must intrinsically account for the emergence of new global features out of local interactions. As the field moves towards chemically and physically complex systems, the structural simplicity of the building blocks will be, once again, a handle to grasp better the meaning of the complex behaviour. This very rich, and largely untouched, road may lead us into completely virgin territory, where new magnetic phases, both static and dynamic can be tested. If the tools of complexity can be applied to molecular magnets, we could use them as a new testground for models of complexity, and we could discover interesting similarities to crowd response, or to the complex dynamics of stock market behaviours.

Acknowledgments

We thank the Humboldt Stiftung (Sofja Kovalevskaja Prize), German DFG, the Baden-Württemberg Stiftung (Kompetenznetz Funkionelle Nanostrukturen), European Research Council (ERC-StG 338258 "OptoQMol") for financial support.

Notes and references

[a] *1. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70550, Stuttgart, Germany. Tel: +49(0)711-685-64907; Fax: +49(0)711-685-64886; E-mail: lapo.bogani@pi1.physik.uni-stuttgart.de*
[b] *Dipartimento di Chimica and INSTM research unit, Università di Firenze, V. della Lastruccia 3, , Sesto Fiorentino (FI), Italy.*

1 R. P. Feynman, *The character of physical laws*, MIT-press, Cambridge **1967**.

2 a) F. Heylighen, *Complexity and self-organization* in Encyclopedia of Library and Information Sciences, Taylor & Francis, **2008**; b) A. Sanjeev, B. Barak *Computational Complexity: a Modern Approach* Cambridge Univ. Press, Cambridge, **2009**.

3 a) D. Grady, C. Thiemann, D. Brockmann *Nature Comm.* **2012**, 3, 864; b) H. Burch, B.Cheswick, Lucent technologies, http://www.lumeta.com/ (accessed in June 2014); c) d) H. Xie, K.-K. Yan, S. Maslov, Physica A, Physica A **2007**, 373, 831-836; e) D. Walker, H. Xie, K.K. Yan, S. Maslov *J. Stat. Mech.* **2007**, 06, P06010

4 a) H. A. Simon, *Rational Decision-Making in Business Organizations* Nobel Prize Lecture, **1978**, available for free online at the website: http://www.nobelprize.org/nobel_prizes/economic-sciences/laureates/1978/simon-lecture.pdf; b) B. I. Carlin, *J Fin Econ*, **2009**, *91*, 278; c) G. Bonanno, F. Lillo, R. N. Mantegna, *Physica A*, **2001**, *299*, 16; d) Center for International Development at Harvard University, *The Atlas of Economic Complexity* **2013** http://www.atlas.cid.harvard.edu; e) C. Castellano, S. Fortunato, V. Loreto, *Rev. Mod. Phys.* **2009**, *81*, 591-646.

5 a) E. Schrödinger, *What is Life? The Physical Aspect of the Living Cell*, Cambridge University Press, Cambridge, USA, **1944**; b) R. Solé, B. Goodwin, *Signs of life: how complexity pervades biology*, Basic books, **2002**; c) Y. Louzouna, S. Solomonc, H. Atland, I. R. Cohen, *Physica A*, **2001**, *297*, 242.

6 E. Dagotto, *Science* **2005**, *309*, 257.

7 a) S. Bogdanovich, D. Popovic, *Phys.Rev.Lett.* **2002**, *88*, 236401; b) J. Burgy *et al., Phys.Rev.Lett.* **2001**, *87*, 277202; c) T. Kimura *et al., Nature* **2003**, *426,* 55.

8 a) G. Alvarez, A. Moreo, E. Dagotto, *Low Temp. Phys.* **2006**, *32*, 290; b) S. Sorella, G. B. Martins, F. Becca, C. Gazza, L. Capriotti, A. Parola, E. Dagotto, *Phys. Rev. Lett.* **2002,** *88*, 117002; c) M. Moraghebi, S. Yunoki, A. Moreo, *Phys. Rev. Lett.* **2002,** *88*, 187001; d) T. Hanaguri *et al., Nature* **2004**, *430,* 1001.

9 a) O. Kahn, *Molecular Magnetism*, WILEY-VCH, Weinheim, **1993**; b) *Magnetism: Molecules to Materials*, Vol.s I-V, (Eds: J. S. Miller, M. Drillon), WILEY-VCH, Weinheim, **2001-2004**; c) *Structure & Bonding*, Vol. 122, (Ed: R.J.P.Winpenny), Springer, Berlin, **2006**; d) D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets* , Oxford University Press, Oxford, **2006**; d) D. Gatteschi, L. Bogani, A. Cornia, M. Mannini, L. Sorace, R. Sessoli, *Solid State Sci.* **2008**, *10*, 1701;

10 a) A. Mydosh, *Spin Glasses: An Experimental Introduction*, Taylor & Francis Ltd, London, **1993**; b) K. H. Fisher, J. A. Hertz, *Spin Glasses*, Cambridge Univ. Press, Cambridge, UK, **1993**; c) K. Binder, A. P. Young, *Rev. Mod. Phys.* **1986**, *58*, 801. d) *Lecture Notes in Physics; Heidelberg colloqium on Spin Glasses,* Vol. 192 (Eds: J. L. Van Hemmen, I. Morgernstern), **1986**; e) L. Bogani *et al.*, submitted.

11 D. J. Amit, H. Gutfreund, H. Sompolinsky, *Phys. Rev. A* **1985**, 32 1007.

12 C. Cervetti, E. Heintze, L. Bogani *Dalton Trans.* **2014**, *43*, 4220-4232.

13 See the volume of the *NATO Advanced Workshop: complexity in Chemistry*, **2013**.

14 a) F. D. M. Haldane, *Phys.Lett.* **1983**, *93A*, 464; b) F. D. M. Haldane, *Phys. Rev. Lett.* **1983**, *50*, 1153; c) F. D. M. Haldane, *J. Appl. Phys.* **1985**, *57*, 3359; d) I. Affleck, *J. Phys. Cond. Matter* **1989**, *1*, 3047.

15 Y. Ajiro, T. Goto, H. Kikuchi, T. Sakakibara, T. Inami, *Phys. Rev. Lett.* **1989**, *63*, 1424.

16 a) D. Luneau, P. Rey, *Coord. Chem. Rev.* **2005**, *249*, 2591; b) A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey *Acc. Chem. Res.* **1989**, *22*, 392; c) L. Bogani, *J. Appl. Phys.* **2011**, *109*, 07B115; d) A. Caneschi, D. Gatteschi, P. Rey, Progress in Inorganic Chemistry, Volume 39 (Ed. S. J. Lippard) Wiley, Hoboken, USA, **2007**.

17 A. Caneschi, D. Gatteschi, M. C. Melandri, P. Rey, R. Sessoli *Inorg. Chem.*, **1990**, *29*, 4228.

18 A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem. Int. Edit.,* **2001**, *40*, 1760.

19 R. Clerac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.*, **2002**, *124*, 12837.

20 a) C. Coulon, H. Miyasaka, R. Clérac*, Structure & Bonding, Berlin,* **2006**, *122*, 163-206; b) L. Bogani, A. Vindigni, R. Sessoli, D. Gatteschi, *J. Mater. Chem.*, **2008**, *18*, 4750.

21 R. J. Glauber *J Math. Phys.* **1963**, *4*, 294.

22 a) L. Bogani, A. Caneschi, M. Fedi, D. Gatteschi, M. Massi, M. A. Novak, M. G. Pini, A. Rettori, R. Sessoli, A. Vindigni *Phys. Rev. Lett.* **2004**, *92*, 207204; b) L. Bogani, *et al. Phys. Rev. B* **2005**, *72*, 064406; c) A. Vindigni, *et al. Appl. Phys. Lett.* **2005**, *27*, 073102; d) J. H. Luscombe *et al., Phys. Rev. E* **1996**, *53*, 5852; e) J. K. Leal da Silva *et al., Phys. Rev. E* **1995**, *52*, 4527.

23 a) L. Bogani, *Ph.D. Thesis*, **2006**; b) L. M. Toma, C. Ruiz-Pérez, J. Pasán, W. Wernsdorfer, F. Lloret, M. Julve, *J. Am. Chem. Soc.* **2012**, *134*, 15265.

24 C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey *Inorg. Chem.*, **1990**, *29*, 4223.

25 a) J. Sinova, G. Canright, A. H. MacDonald, *Phys. Rev. Lett.* **2000**, *85*, 2609-2612; b) C. Reichhardt, C. J. Olson-Reichhardt, *Phys. Rev. B,* **2011**, *84*, 174208; c) K.Takahashi, Y. Matsuda, *J. Phys.: Conf. Ser.,* **2011**, *297*, 012021; d) T. M. Nieuwenhuizen, F. Ritort, Physica A, **1998**, *250*, 8-45.

26 a) M. A. Ruderman, C. Kittel, *Phys. Rev.* **1954**, *96*, 99; b) T. Kasuya, *Prog. Theor. Phys. Kyoto* **1956**, *16*, 45; c) K. Yoshida, *Phys. Rev.* **1957**, *106*, 893; d) J. Jensen, A.R. Mackintosh, *Rare Earth Magnetism: Structures and Excitations*, Clarendon Press, Oxford, **1991**.

27 J. Villain *Ann. Isr. Phys. Soc.* **1978** 2 565.

28 F. Cinti *et al. Phys. Rev. Lett.* **2008**, 100, 057203.

29 T. Masuda, A. Zheludev, A. Bush, M. Markina, A. Vasiliev, *Phys. Rev. Lett.* **2004**, *92*, 177201.

30 A. Abragam, B. Bleaney, *Electron paramagnetic resonance of transition ions*, Clarendon Press, Oxford, **1970**.

31 a) P. C. Hohenberg, B. I. Halperin *Rev. Mod. Phys.* **1977**, *49*, 435; b) M. P. Nightingale, H. W. J. Blöte *Phys. Rev. Lett.* **1996**, *76*, 4548.

32 a) J. Bardeen, L. Cooper, R. Schrieffer, *Phys. Rev.* **1957**, *108*, 1175; b) W. de Heer *Rev. Mod. Phys.* **1993**, *65*, 611.

33 a) R. Dynes, P. Sharifi, J. Valles in *Lattice Effects in High Tc Superconductors*, (Eds: Y. Bar-Yam, T. Egami, J. Mustre-Leon, A. Bishop), World Scientific, Singapore, **1992**; b) G. R. Stewart *Rev. Mod. Phys.* **2011**, *83*, 1589; c) N. P. Armitage, P. Fournier, R. L. Greene, *Rev. Mod. Phys.* **2010**, *82*, 2421.

34 R. J. Bursill, R. H. McKenzie, C. J. Hamer, *Phys. Rev. Lett.* **1999**, *83*, 408; b) A. W. Sandvik, D. K. Campbell, *Phys. Rev. Lett.* **1999**, *83*, 195; c) A. B. Sushkov, O. Tchernyshyov, W. Ratcliff II, S. W. Cheong, H. D. Drew, *Phys. Rev. Lett.* **2005**, *94*, 137202.

35 L. Bogani *et al. Adv. Mater.* **2007**, *19*, 3906–3911.

36 C. Cervetti *et. al. submitted* **2014**.

37 a) J. Albert, E. M. Chudnovsky, D. A. Garanin, *Phys. Rev. B* **2006**, *74*, 115102; b) C. Calero, E. M. Chudnovsky, D. A. Garanin *Phys. Rev. B* **2006**, *74*, 94428.

38 a) L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179-186; b) S. Sanvito, A. R. J. Rocha, *J. Comp. Theor. Nanosci.* **2006**, *3*, 624-642; c) A. R. Rocha1, V. M. García-suárez, S. W. Bailey, C. J. Lambert, J. Ferrer, S. Sanvito *Nat. Mater.* **2005**, *4*, 335-339; d) S. Sanvito, *Chem. Soc. Rev.* **2011**, *40*, 3336-3355; e) S. D. Jiang, K. Goβ, C. Cervetti, L. Bogani, *Sci. China Chem.* **2012**, *55*, 867-882.

39 a) L. Bogani, W. Wernsdorfer, *Inorg. Chim. Acta* **2008**, *361*, 3807; b) L. Bogani, C. Danieli, E. Biavardi, N. Bendiab, A. L. Barra, E. Dalcanale, W. Wernsdorfer, A. Cornia, *Angew. Chem. Int. Ed.* **2009**, *121*, 760; c) S. Kyatskaya, J. R. G. Mascarós, L. Bogani, F. Hennrich, M. Kappes, W. Wernsdorfer, M. Ruben, *J. Am. Chem. Soc.*, **2009**, *131*, 15143.

40 a) R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties Of Carbon Nanotubes*, World Scientific Press, Singapore, **1998**; b) J.-C. Charlier, X. Blase, S.Roche, *Rev. Mod. Phys.* **2007**, *79*, 677.

41 a) A. H. Castro Neto, F. Guinea, N. M. Peres, K. S. Novoselov, A. K. Geim *Rev. Mod. Phys.* **2009**, *81*, 109; b) V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, A. H. Castro Neto *Rev. Mod. Phys.* **2012**, *84*, 1067; c) K. S. Novoselov *et al*. *Science* 2**004**, *306*, 666.

42 a) M. N. Baibich, J. M. Broto, A. Fert, F. N. V. Dan, F. Petroff, *Phys. Rev. Lett.* **1988**, *61*, 2472; b) G. Binasch, P. Grünberg, F. Saurenbach, W. Zinn, *Phys. Rev. B* **1989**, *39*, 4828.

43 C. Felser, G. H. Fecher, B. Balke, *Angew. Chem. Int. Ed.* **2007**, *46*, 668.

44 a) A. Liang, M. P. Shores, M. Bockrath, J. R. Long, *Nature* **2002**, *417*, 725; b) C. Romeike, M. R. Wegewijs, W. Hofstetter, H. Schöller, *Phys. Rev. Lett.* **2006**, *97*, 206601; c) M. N. Leuenberger, E. R. Mucciolo, *Phys. Rev. Lett.* **2006**, *97*, 126601.

45 J. Park, *et al. Nature* **2002**, *417*, 722–725.