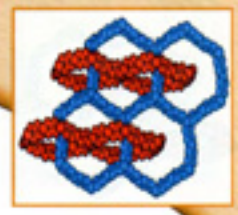


Des aimants moléculaires aux molécules magnétiques

Dante Gatteschi*, professeur

Résumé Les molécules comportant un grand nombre d'ions de transition magnétiques peuvent donner naissance à une hystérésis magnétique d'origine moléculaire. Ce phénomène nouveau a été observé par exemple dans deux molécules ayant respectivement douze ions manganèse et huit ions fer. Une vue d'ensemble de ces molécules est présentée dans cet article, qui montre comment, en principe, il peut devenir possible de stocker de l'information sur une seule molécule.

Summary **From molecular magnets to magnetic molecules**
Molecules comprising a large number of magnetic transition metal ions may give rise to magnetic hysteresis of molecular origin. This new phenomenon has been observed for instance in two molecules comprising twelve manganese and eight iron ions respectively. The properties of these molecules are reviewed here, showing how in principle it may be possible to store information in one single molecule.

Mots-clés Molécules à haut spin, molécules-aimants, bistabilité.
Key-words High spin molecules, single molecule magnets, bistability.

Magnetochemistry is that branch of chemistry which traditionally measures magnetic properties, mainly paramagnetic properties, in order to obtain structural information [1]. The key for understanding the origin of the structural information contained in the magnetic properties of a compound is that first of all it is generally possible to easily obtain the number of unpaired electrons present, and with some more labour also the chemical environment in which the paramagnetic center is located. In this respect the technique has essentially been used for transition metal compounds, because the magnetic properties of organic radicals and rare earth ions, for different reasons, are not much sensitive to the environment. Magnetochemistry has also been largely used in order to obtain structural information in metallo-proteins and metallo-enzymes.

In the last few years however there has been a complete change in interest moving to the design and synthesis of new materials for new magnetic properties. In particular simple paramagnets have no longer been the focus of interest, which has shifted to molecular materials with permanent magnetization, to two- and one-dimensional magnetic materials [2]. All these compounds have the common feature of requiring the control of infinite arrays of magnetic centers, while in simple paramagnets the individual centers are independent one from the other. Therefore magnetochemistry is now a more complete branch of chemistry, in which clever design, ingenious synthesis and sophisticated physical techniques, simply undreamed of just few years ago, must coexist in order to give new classes of materials. For sure the transition has not been the initiative of a single scientist, but I have no doubt in indicating Olivier Kahn as the single individual who has most contributed to the development of the field of magnetic molecular materials, with his creativity, imagination, contagious enthusiasm, synthetic ability, and mastering of complex experimental and theoretical techniques.

The first challenge of the renovated magnetochemistry has been that of synthesizing molecular ferromagnets, or, better, molecule based systems which have spontaneous magnetization below a critical temperature. In order to do this it is necessary to choose appropriate magnetic building blocks, and connecting them properly using suitable synthetic strategies. The conditions for a ferromagnet are stringent, because it is well known that molecules containing unpaired electrons tend to form bonds with pairing of the spins. Olivier Kahn has certainly given a large contribution showing on one side which strategies can be used to overcome this difficulty, and on the other how it is possible to take advantage of difficulties, by developing the so-called ferrimagnetic strategy. In this case it is possible to obtain a spontaneous magnetization by using two different building blocks, containing different numbers of unpaired electrons: even if bonds are formed, some unpaired electron will be left, thus giving rise to spontaneous magnetization.

Certainly it is not the goal of this article to resume all the fundamental results obtained by Olivier Kahn, but his contributions have been seminal both on the theoretical and the experimental side. In the former his model has been a clever translation into the molecular orbital language of the '80's of the rules for obtaining parallel or antiparallel arrangement of the individual magnetic moments of the molecular building blocks. All the experimentalists have

* Department of Chemistry, University of Florence, Via Maragliano 77, I-50144 Florence, Italy.
Tel. : 0039 055362551. Fax : 0039 055354845. E-mail : gattesch@chim1.unifi.it

Magnétisme moléculaire

Un hommage à Olivier Kahn

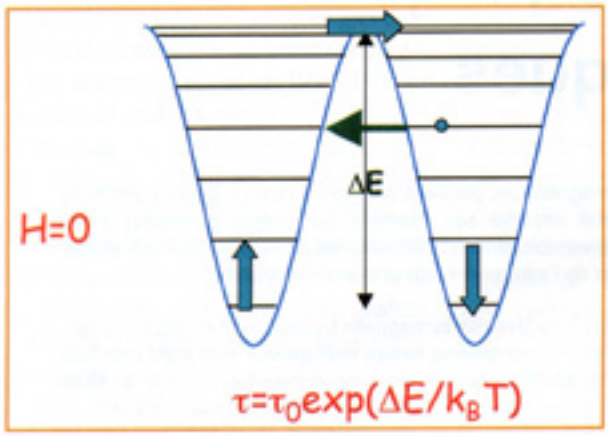


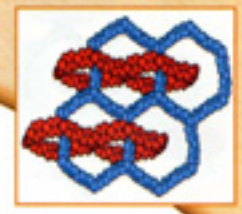
Figure 1 - Energy level diagram for a spin system characterized by the spin quantum number S in the absence of a magnetic field. On the left well are shown the levels with $0 \leq M \leq S$, on the right those with $-S \leq M \leq 0$. The wide arrows indicate the magnetization corresponding to the indicated levels. The fine arrow indicates that the tunnelling process is allowed. Refer to the text for more detail.

now a clear and simple guide for synthesizing their complex molecules and for rationalizing their magnetic properties. On the experimental side he reported some of the first molecular ferrimagnets, managed to obtain a fully interlocked structure containing three different magnetic centers, reported molecular magnets with high coercive field (hard magnets).

Another field where he showed the creative role of his imagination was in the old field of spin crossover materials. These are compounds originally reported in Italy before the second world war, which have the characteristics of having low magnetization at low temperature, and high magnetization at high temperature. The transition from one spin state to the other may occur either gradually or abruptly, and in the latter case with or without hysteresis. The presence of a hysteresis cycle is particularly exciting because at the same temperature the material can be in one state or the other, depending on the history of the sample. In this way it is possible to store information in the material. Olivier Kahn was able to synthesize a material with the hysteresis cycle centered around room temperature, opening the possibility of exciting applications.

A more recent field of molecular magnetism, in which Olivier Kahn did not really enter is that of Single molecule magnets, SMM [3-6]. I must confess that I am embarassed to use this term, because Olivier Kahn did not like it, and was contrasting its use in every seminar or conference where it was used. I admit that he was right: the term is not correct, and should not be used, but it has the advantage of being evocative and catching the attention. In fact many terms which are currently used in science now have similar features. Anyway, SMM's are molecules containing a large number of magnetic centers, whose magnetization relaxes so slowly at low temperature that the molecules remain permanently magnetized for long times. Let me try to be more clear. In a paramagnet the magnetization, which one can easily visualize as a vector (a pointed arrow), is not fixed like in a bulk magnet. Actually, if it is forcedly oriented along a given direction by applying an external magnetic field, it will rapidly go back to equilibrium when the field is removed. Going back to equilibrium means that the average magnetization must go to zero, because a paramagnet has no permanent magnetization. At high temperature the magnetization of a paramagnet, characterized by a spin S, corresponding to half the number of unpaired electrons, is zero because an individual spin passes rapidly through all the possible projections, $-S \leq M \leq +S$, and there is no interaction between the various magnetic centers. However at low temperature matters may become different. Let us imagine that two of the projections, say those characterized by $M = \pm S$, become more energetically favourable than all the others, in the absence of an applied magnetic field. A possible case is shown in *figure 1* for $S = 10$. The fact that the M states group in pairs in energy, with the exception of the $M = 0$ state, is due to the coupling of the spins to the orbital motion of the electrons, and through this they feel that in this particular case it is more convenient to align parallel to the symmetry axis of the molecule. In magnetic jargon this is equivalent to easy axis type magnetic anisotropy. At low temperature the molecules will go into the lowest $M = \pm 10$ level, and the magnetization is zero, because there will be equal numbers of molecules with magnetization corresponding to $M = -10$ and $M = +10$. If a field is applied parallel to the easy axis, the magnetization of all the molecules will orient parallel to the field, and the magnetization becomes different from zero. In the quantum description of the S spin this corresponds to preparing all the molecules in the state $M = -10$, as shown in *figure 2*. When the field is switched off, the scheme of the allowed energy levels is again that of *figure 1*. The two levels $M = -10$ and $M = +10$, will have to be equally populated, but in order to do that a molecule which initially is characterized by $M = -10$ must change first to $M = -9$, then to $M = -8$, up to $M = 0$, and then down to the positive M values. In energy terms it must climb a barrier, corresponding to the energy difference in zero field between the $M = -10$ and the $M = 0$ level. The anisotropy barrier can be as high as 70 K in

MAGNÉTISME MOLÉCULAIRE
UN HOMMAGE À OLIVIER KAHN



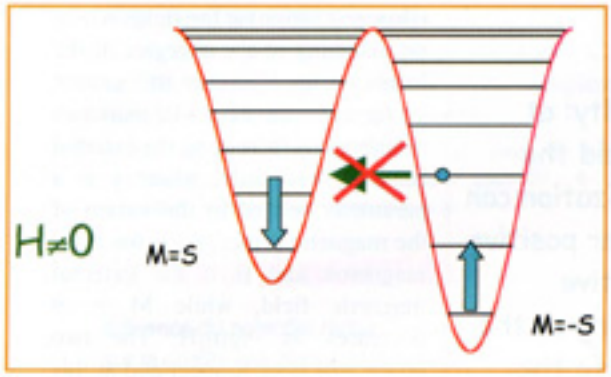


Figure 2 - Energy level diagram for a spin system characterized by the spin quantum number S in the presence of a magnetic field H. On the left well are shown the levels with $0 \leq M \leq S$, on the right those with $-S \leq M \leq 0$. The vertical arrows indicate the magnetization corresponding to theindicated levels. The crossed arrow indicates that the tunnelling process is forbidden. Refer to the text for more detail.

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$. $Mn_{12}Ac$, the first discovered SMM, whose structure is shown in *figure 3*. It comprises an external ring of eight manganese(III) ions, each with spin S = 2, and an internal tetrahedron of four manganese(IV), each with S = 3/2. The individual spins are coupled as schematically shown in *figure 3*. In the ground state all the manganese(III) spins are parallel to each other, giving a resulting spin S = 16, and antiparallel to the manganese(IV) spins. The latter give a resulting spin S = 6, which, subtracted from S = 16 gives a total spin S = 10. Several different experimental techniques show that the ground S = 10 is split as shown in *figure 1*. Therefore the magnetization of $Mn_{12}Ac$ should behave as indicated above for the ideal case. In particular if the relaxation time of the magnetization is measured as a function of temperature a nice Arrhenius plot is observed [5]. In fact, since the relaxation of the magnetization follows a thermally activated behavior the corresponding time must be given by:

$$\tau = \tau_0 \exp(\Delta/kT) \qquad (1)$$

where $\tau_0 = 2.1 \times 10^{-7}$ s, and $\Delta/k = 62$ K.

Using equation (1) and the experimentally determined parameters τ_0 and Δ the relaxation time at 2 K is 6.1×10^6, ca. 70 days. We can say that the relaxation time is of the order of the month. This means that if the molecule is magnetized, by applying an external field, when the field is removed after one month the residual magnetization will be about 50 % of the initial one. Therefore $Mn_{12}Ac$ behaves like a magnet, because it has a non-zero magnetization also in the absence of an applied field. It must be stressed that even if these molecules are called SMM, so far no single molecule experiment has been reported and all the measurements have been performed on assemblies of molecules. This has been made possible by the fact that the molecules are all identical to each other. $Mn_{12}Ac$ crystallizes in a tetragonal space group and all the molecules are isooriented. This is indeed a great advantage over other types of magnetic particles, which are very difficult to be made as monodisperse assemblies. In fact $Mn_{12}Ac$ was the right molecule at the right time. In fact there was a large interest in the investigation of possible quantum effects in the relaxation of the magnetization in mesoscopic objects [7]. This field followed an original suggestion by Leggett, and had been widely developed on the theoretical side. However experimental evidence was lacking. In fact quantum effects depend exponentially on the size of the magnetic particles, and unless absolutely monodisperse assemblies are available, sophisticated measurements on individual particles must be performed.

$Mn_{12}Ac$ shows a typical stepped hysteresis, which has been taken as the first evidence of quantum tunneling of the magnetization [8,9]. But let us proceed step by step. The first point to comment is that a hysteresis cycle is observed. This is observed also in bulk magnets, and in fact it is widely used, in particular for storing information. The origin of the hysteresis is irreversible phenomena associated to the movement of the walls separating different magnetic domains. In $Mn_{12}Ac$ the origin is completely different, it is due to the slow molecular relaxation. In fact, the measurements are performed by first applying a strong field and then gradually reducing it. If one spends a very long time in measuring each point, the system has enough time to reach equilibrium which corresponds to zero magnetization.

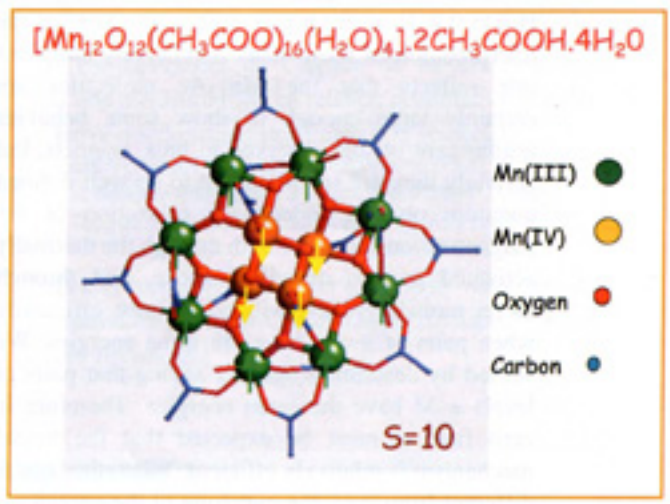
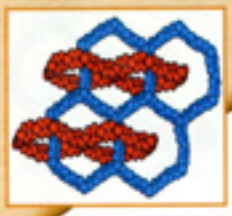


Figure 3 - Structure of Mn12Ac. The arrows indicate the preferred spin orientation in the ground state. The crystals are tetragonal and the cluster has S_4 symmetry.



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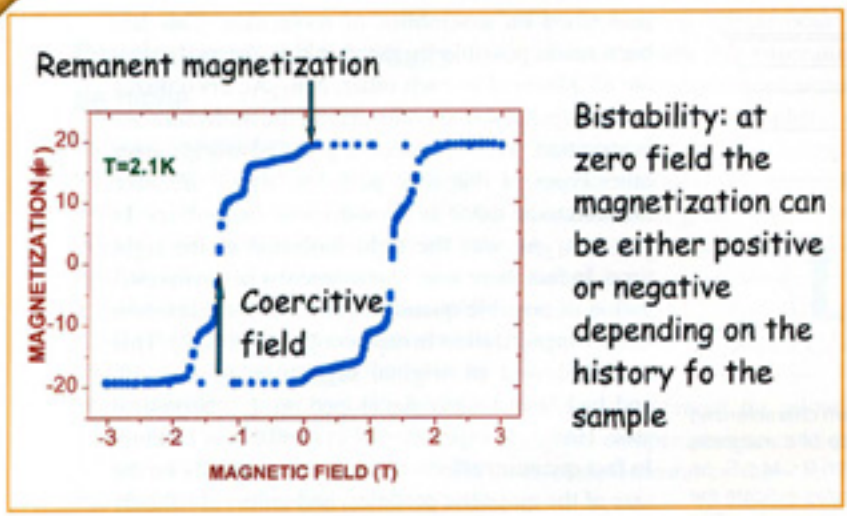

Figure 4 - Magnetic hysteresis loop for a single crystal of Mn12Ac with the external magnetic field parallel to the tetragonal axis.

This means that at low temperature one should spend a few months for each point, which is clearly difficult to be achieved. However, if only a few minutes are spent on each point then the magnetization does not have time to go to zero and only slightly decreases. In this way a hysteresis cycle is observed as shown in *figure 4*. In particular it is seen that at zero field the magnetization can be either positive or negative, depending on the history of the sample. This means that the molecules are bistable, and bistability is widely used for storing information. Now this opens the interesting perspective of storing information in a single molecule.

Looking in detail the hysteresis curve of $Mn_{12}Ac$ one sees some steps. In the cycles measured at different temperatures the steps occur always at the same field. In particular steps are observed at H = n 0.4 T, where n = 0, 1, 2,...The key for the interpretation of these steps is relatively simple if one reflects that the $Mn_{12}Ac$ molecules are certainly large enough to show some behavior reminiscent of that observed in bulk magnets, but certainly they are small enough to be well defined quantum objects. Indeed the relaxation of the magnetization can occur both through the thermally activated process described above, and through direct tunneling. This will occur most efficiently when pairs of levels have the same energies. We started by describing *figure 1* saying that pairs of levels ± M have the same energies. Therefore in zero field it must be expected that the tunnel mechanism is relatively efficient. When the field is different from zero, the matching of the energies is lost, the M = +10 will have a different energy from M = -10, the tunneling becomes less efficient. In fact the hysteresis cycle shows flat regions (slow relaxation) at the fields where no matching of the energies of the levels occur. However this cannot go for ever: the M = +10 increases its energy on increasing the external field, as $+10g\mu_B H$, where g is a parameter related to the nature of the magnetic center, μ_B is the Bohr magneton and H is the external magnetic field, while M = -9 decreases as $-9g\mu_B H$. The two levels will have to meet and at this field the conditions for tunneling are restored. The knowledge of the energy levels of *figure 1* shows that these crossings occur at fields H = n 0.4 T in excellent agreement with the experimental data. The tunneling phenomena occur between pairs of levels which are thermally populated. For this reason the process has been termed thermally assisted quantum tunneling.

There is one question I have not taken into consideration so far, but which might be present in the mind of many readers: are you sure that the observed behavior is a molecular one, and not associated with some transition in the solid state? There is now convincing evidence, including specific heat measurements, but the most elegant is the observation of MCD spectra in solution without an applied field. MCD spectra measure the different absorption of right and left circularly polarized light in the presence of an applied magnetic field. When the MCD spectra of $Mn_{12}Ac$ were recorded in frozen solution they were found to be persistent when the field was removed. Further the sign of the differential absorption at zero field depended on the history of the sample. Therefore a hysteresis was observed in solution, ruling out the possibility of cooperative phenomena. Slow relaxation of the magnetization of $Mn_{12}Ac$ therefore is a genuine molecular phenomenon.

After $Mn_{12}Ac$ there have been several variations, starting from the most obvious ones which used different carboxylates or partially reduced the manganese ions. The latter category has provided some yet not resolved puzzle. If one electron is added to the Mn_{12} cluster a species containing one manganese(II), seven manganese(III), and four manganese(IV) is obtained, with a ground state S = 19/2. Although genuine quantum tunneling should not be observed in a system with an odd number of unpaired electrons, the hysteresis curve shows a marked step at zero field. More work is needed in this area.

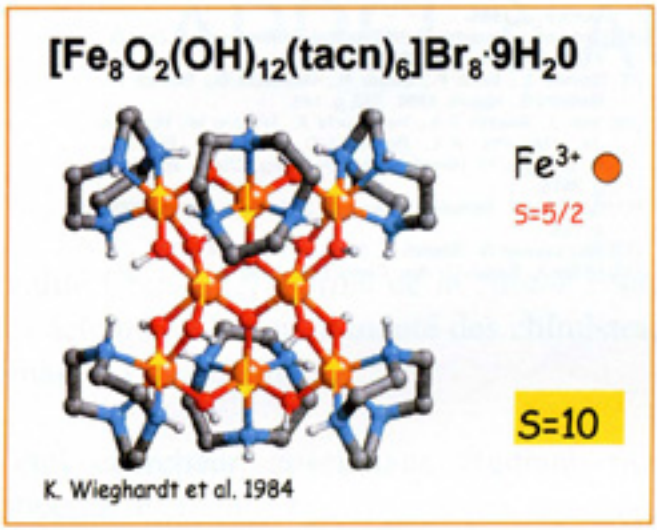

Figure 5 - Structure of Fe8. The arrows indicate the preferred spin orientation in the ground state.

Other examples of SMM have been found in Mn_4, Fe_4, $CrMn_6$, V_4 species [9]. These compounds show that in order to observe slow paramagnetic relaxation even small numbers of magnetic centers may be sufficient, provided that a relatively large spin state with a suitable barrier is present, with easy axis type magnetic anisotropy. However the second most investigated cluster is an octanuclear iron(III) complex, $[Fe_8O_2(OH)_{12}(tacn)_6]Br_8{\cdot}9H_20$, Fe_8, where tacn = 1,4,7-triazacyclononane [10]. Fe_8 has the structure shown in *figure 5*. It has the same S = 10 ground state of $Mn_{12}Ac$, which can be simply justified by splitting the set of eight iron(III), S= 5/2, ions into two subsets, one of 6 up spins and 2 down spins. This qualitative assignment has been confirmed by polarized neutron experiments which have photographed a spin density corresponding to the above description. The barrier for the reorientation of the magnetization in Fe_8 is about one third of that observed in Mn_{12}. Correspondingly the slow relaxation of the magnetization and the hysteresis of Fe_8 is observed at lower temperature compared to $Mn_{12}Ac$. The other interesting feature of Fe_8 is that, while $Mn_{12}Ac$ has tetragonal symmetry, it has no symmetry at all. This means that the magnetization encounters a barrier not only when it must go from +z to –z, but also when it moves in the xy plane. In order to have under-barrier tunneling the presence of a transverse field is of paramount importance. On the ground of molecular symmetry alone it can be expected that the tunneling mechanism is much more efficient in Fe_8 than in $Mn_{12}Ac$, and this is borne out by experimental data. In fact, while the relaxation of the magnetization of $Mn_{12}Ac$ becomes extremely long at low temperature, and the pure tunneling regime is never attained, in Fe_8 the relaxation time never becomes too long, and evidence of the pure tunneling regime, namely temperature independence of the magnetic relaxation, is obtained below 250 mK.

The SMM are becoming a true gold mine for observing quantum phenomena, and somebody is thinking about the possibility of using them in order to store information for quantum computing. For instance it had long been predicted that the so-called Berry phase could be observed in magnets. If a variable transverse field, i.e. perpendicular to the easy axis, is applied the so called tunnel splitting is observed to oscillate. The tunnel splitting is the separation of the M = ±10 levels, determining the tunnel phenomenon. In semi-classical treatment the splitting is due to the movement of two magnetic vectors, one clock- and the other anticlock-wise.

The conclusion one can reach is that molecular techniques are now providing much new physics, especially in the extremely vivacious field of nanostructures, where it can be expected to observe coexistence of quantum and classical behaviors. The limitations so far have been associated with the difficulties of growing larger clusters, but many ingenious chemists are operating and each month new larger molecules are synthesized. The best achievements so far have been obtained with non-magnetic metal ions: Müller recently reported a cluster comprising 256 molybdenum ions [11], and the same group was able to embed in another molybdenum cluster 30 magnetic iron(III) ions. The latter has an appealing quasi spherical structure, with an S= 0 ground state. However the separation from the first excited state must be extremely small, because the magnetization does not show any anomaly even at very low temperatures. In this sense the cluster can be considered as a tiny piece of a bulk antiferromagnet, with a behavior which corresponds to a classical rather than to a quantum object.

It is easy for me to predict that in the next few years many more large magnetic clusters will be reported, going closer and closer to the bulk limit, and chemists will be more and more involved in learning how to dewsign complex magnetic objects. For sure all these achievements have been made possible by the enthusiastic work of a great scientist, Olivier Kahn.

Acknowledgements

The financial support of the Research Network Molnanomag, HPRNCT-1999-00012, is gratefully acknowledged.

MAGNÉTISME MOLÉCULAIRE
UN HOMMAGE À OLIVIER KAHN

References

[1] Carlin R.L., *Magnetochemistry*, Springer-Verlag, Berlin, **1986**.
[2] Kahn O., *Molecular Magnetism*, Wiley-VCH, New York, **1993**.
[3] Sessoli R., Gatteschi D., Caneschi A., Novak M.A., *Nature*, **1993**, *365*, p. 141.
[4] Gatteschi D., Caneschi A., Pardi L., Sessoli R., *Science*, **1994**, *265*, p. 1054.
[5] Christou G., Gatteschi D., Hendrickson D.N., Sessoli R., *MRS Bulletin*, **2000**.
[6] Aubin S.M.J., Wemple M.W., Adams D.M., Tsai H.-L., Christou G., Hendrickson D.N., *J. Am. Chem. Soc.*, **1996**, *118*, p. 746.
[7] *Quantum Tunneling of Magnetization QTM '94*, Gunther L., Barbara B., Eds. NATO ASI Ser. E, *vol. 301*, Kluwer, Dordrecht, **1995**.
[8] Friedman J., Sarachik M.P., Tejada J., Maciejewski J., Ziolo R., *Phys. Rev.Lett.*, **1996**, *76*, p. 3820.
[9] Thomas L., Lionti F., Ballou R., Gatteschi D., Sessoli R., Barbara B., *Nature*, **1996**, *383*, p. 145.
[10] Yoo J., Brechin E.K., Yamaguchi A., Nakano M., Huffman J.C., Maniero, A.-L. Brunel, L.C. Awaga, K. Ishimoto, H. Christou, G. Henrdickson, D.N. *Inorg. Chem.*, **2000**, *39*, p. 3615.
[11] Gatteschi D., Sessoli R., Cornia A., *JCS Chem. Comm.*, **2000**, p. 725.
[12] Wernsdorfer W., Sessoli R., *Science*, **1999**, *284*, p. 133.
[13] Müller A., Serain C., *Acc. Chem. Res.*, **2000**, *33*, p. 2.