Russian Chemical Bulletin, International Edition, Vol. 60, No. 12, pp. 2439—2442, December, 2011

Reviews

Molecular ferromagnets*

A. L. Buchachenko

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Acad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: abuchach@chph.ras.ru

An analysis of magnetism of nanochemical systems opens new routes to fabrication of ferromagnets from diamagnetic substances and new principles of constructing molecular ferromagnets, hybrid magnetic materials, and single-molecule magnets based on high-spin molecules and complexes. The use of such systems in spin computing is considered.

Key words: molecular ferromagnets, single-molecule magnets.

Ferromagnets belong to materials that constitute the foundation of modern civilization. Until recently, one could distinguish two types of ferromagnets, *viz.*, metallic (iron, cobalt, Co_5Sm-type alloys, *etc.*) and ionic ones (Fe_3O_4, $CoFe_2O_4$, etc.). In both of them, the carriers of magnetism are atoms (or ions) of metals with partially filled inner d- or f-electron shells; this means that a number of d- or f- electrons have unbalanced angular momenta (spins); it is these electrons that are responsible for magnetism.

At the end of the 20th century, a new, third type of ferromagnets appeared, *viz.*, molecular ferromagnets built of radicals. This was the first breakthrough to organic ferromagnets. It was followed by the next breakthrough, the synthesis of stable polyradicals and paramagnetic complexes in which metal ions (carriers of magnetism) are surrounded by a ligand shell comprised of organic molecules. Chemists learned to produce a variety of such materials with high spin density. Molecules and organometallic complexes in which each chemically individual species bears a few tens of unpaired electrons have been synthesized. High-spin complexes with more than a hundred of unpaired electrons are now available.

Molecular ferromagnetism

Radicals and paramagnetic complexes have always been "home affairs" of chemistry. Only the synthesis of high-spin molecules brought them beyond the scope of the chemical science into new hi-tech fields. The main problem on the road to molecular ferromagnets is to answer the question of how to produce a ferromagnetic substance from a paramagnetic molecular material.

In the spin molecules, the unpaired electrons are on the outer s and p atomic orbitals, *i.e.*, occupy the "surface"

---

* Dedicated to Academician of the Russian Academy of Sciences R. Z. Sagdeev on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2393—2396, December, 2011.

of electron shells. For them, intermolecular exchange interaction is negative and arranges the electron spins antiparallel, *i.e.*, creates a low-spin antiferromagnetic substance from a high-spin ferromagnetic material. Thus, one has to solve a paradoxical problem of obtaining a ferromagnetic substance through antiferromagnetic interaction.

This problem was solved successfully. The paradox can be solved using two physicochemical models.

One of them is based on the interplay of the signs of the electron spin density. Usually, a spin is distributed over the entire molecule and "visits" all atomic orbitals with a higher or lower probability either by the spin delocalization mechanism, thus bringing a positive spin density, or by the spin polarization mechanism, thus bringing a negative spin density to atoms (in this case, the spin density is oriented opposite to the total spin of the molecule).

Let the spin densities on the atoms *i* and *j* in the spin molecules A and B, respectively, be ρ_i and ρ_j. The total energy of exchange interaction between the molecules A and B (it is this energy that lines spins up) is

$$H = -JS_{\rm A}S_{\rm B}, \tag{1}$$

where $S_{\rm A}$ and $S_{\rm B}$ are the spins of the molecules A and B, respectively, and J is the total exchange potential (here, energy is written in the operator form). The energy in Eq. (1) can be represented by the sum of pair interactions between the atoms *i* and *j* in terms of the spins of these atoms $S_i^{\rm A}$ and $S_i^{\rm B}$, respectively:

$$H = -\sum_{ij} J_{ij} S_i^{\rm A} S_j^{\rm B}. \tag{2}$$

The spin on an atom can be expressed using the spin density as $S_i^{\rm A} = S^{\rm A}\rho_i$ and $S_j^{\rm B} = S^{\rm B}\rho_j$. Then, from Eq. (2) it follows that

$$H = -S^{\rm A}S^{\rm B}\sum_{ij} J_{ij}\rho_i\rho_j. \tag{3}$$

A comparison of expressions (3) and (1) gives

$$J = \sum_{ij} J_{ij}\rho_i\rho_j. \tag{4}$$

Thus, the total exchange potential J is given by the sum of potentials of pair exchange interactions between the atoms *i* and *j* with the spin densities ρ_i and ρ_j.

Equation (4) is key to the explanation. Indeed, even with antiferromagnetic exchange interaction ($J_{ij} < 0$) one can obtain ferromagnetic arrangement of spins ($J > 0$) if the spin molecules are lined up in the crystal in such a way that atoms of the molecule A with the positive spin density be in contact with atoms of the molecule B with the negative spin density ($\rho_j\rho_j<0$). Two spin sublattices with positive and negative spin densities thus appear in such a crystal. But since the positive spin densities are one or two orders of magnitude higher than the negative spin densities, the magnetization of the first sublattice is much higher than the balancing magnetization of the second sublattice, which eventually makes the crystal macroscopically ferromagnetic.

This model was for the first time proposed by McConnell[1] in 1963, but it was out of demand for long. The first true organic ferromagnet containing no metal atoms whose molecular and crystal structures exactly corresponded to the McConnell model was obtained only in 1989. This gave an impetus to experimental search for novel organic ferromagnets.[2–5]

A reliable proof of this mechanism of generating ferromagnetism was obtained from analysis of the interaction of two radicals, allyl $CH_2{-}^{\bullet}CH{-}CH_2$ and methyl $^{\bullet}CH_3$.[6] In the former, positive π-electron spin density of the unpaired electron is distributed between the terminal carbon atoms (each of them bears a spin density of about 0.51) while the spin density on the central carbon atom is negative, namely, –0.02. When methyl adds to the terminal carbon atoms of allyl, the electron spins of both radicals are aligned antiparallel (antiferromagnetic interaction). This corresponds to the formation of a chemical bond. But if the methyl radical adds to the central atom of allyl, the electron spins of both radicals are aligned parallel (ferromagnetic interaction). This is in excellent agreement with Eq. (4), *viz.*, ferromagnetic alignment of spins ($J > 0$) is attained in spite of antiferromagnetic interaction between CH_3 and the CH fragment of allyl ($J_{ij} < 0$) where one has $\rho(CH_3) > 0$ and $\rho(CH) < 0$.

The other model for molecular ferromagnetism assumes metal ions with different spins and magnetic moments as building units for molecular complexes. By cocrystalization or using chemical reactions between complexes of low-spin and high-spin metal ions (*e.g.*, Cu and Fe, Cu and Mn, Cu and Cr, Cu and Ni, Cu and Gd, *etc.*) one can obtain crystals with regularly alternating positions of the high-spin and low-spin complexes. Then, at negative intermolecular exchange interaction, two magnetic sublattices appear in the crystal, a high-spin sublattice of the complexes with Fe, Cr, Mn, Ni, Gd, *etc.* ions and a low-spin sublattice containing, for example, copper complexes. Since the magnetization of the first sublattice is much higher than that of the second sublattice, the entire molecular crystal becomes ferromagnetic. This is the so-called Buchachenko—Yamaguchi model.[7] A huge number of molecular ferromagnets were obtained on its basis.[5,8]

Molecular structures of ferromagnets are as diverse as methods of their synthesis. High-spin molecules or complexes can form clusters, linear chains or planar (2D) structures. Spin alignment within a structural fragment is governed by exchange interaction, while spin alignment within a system of clusters, chains, and 2D structures is attained through exchange or magnetic dipole interaction.

They cannot, however, compete as magnetic materials with classical ferromagnets because of two essential drawbacks. One of them is genetically programmed, namely, the electron spin density is low and there is a large amount of spinless ballast. The low spin density means long distances between neighboring spins and weak spin-spin exchange interaction. It is this exchange interaction that is responsible for magnetism. That is why the ferromagnet—paramagnet transition temperatures are so low (usually, they are in the range 3—30 K).

A direct route to strong (high-temperature) molecular magnets is to get rid of spinless ballast and increase the spin density by using "small" radicals and ligands (*e.g.*, sulfide, disulfide, sulfoxide, phosphide, phosphate, cyanide, and nitroxide fragments). However, by doing so one can lose ferromagnetism *per se*. The reason is that exchange interaction in high-spin molecules and complexes, which involves unpaired electrons occupying outer electron shells, is almost always negative and creates an antiferromagnetic spin alignment.

Nanomagnets

Interest in nanomagnets is due to a rising tide of interest in nanochemistry. Classical nanomagnets are particles a few hundreds of nanometers in size. They are usually prepared by dispersion or precipitation of ferromagnetic materials and are therefore nonuniform and characterized by some particle size and magnetic moment distributions of nanoparticles. Actually, nanomaterials built of such nanomagnets inherit ferromagnetism of their precursors.

A different approach is to fabricate nanoferromagnets from diamagnetic materials. The idea is as follows. In small clusters, where the fractions of the surface and volume atoms or ions are commensurable, their exchange potentials in the bulk and on the surface are unbalanced. As a result, the magnetic moments of internal atoms are not balanced by the surface magnetic moments and small clusters thus acquire magnetism. For instance, clusters of diamagnetic MnF_2 30—50 nm in size become magnetic. Chromium clusters 40—70 nm in size are also magnetic, although bulk chromium is not. The 10-nm $MnFe_2O_4$ and 2-nm CoRu nanoparticles are also magnetic, although their macroscopic precursors are not.[9] CoRh, PtPd, and $Mn_{55}Pt_{45}$ alloys are non-magnetic, but their clusters have strong magnetic properties. Strong magnetism appears in a GaAs nanowire doped with Mn (1—5%) and in Eu_6C_{60}, Eu_3C_{70}, and Eu_9C_{70} nanoclusters. Ferromagnetism is a universal property of both organic (carbon, graphite), and inorganic nanoparticles.[10] Transformation of paramagnets or antiferromagnets into ferromagnets through nanochemistry is a promising route to ferromagnetic materials.

Depending on their size, nanomagnets can be monodomain or multidomain. The scale boundary between them is determined by the ratio between the energy of exchange interaction which lines up spins and the energy of dipole interaction which divides spins into groups (domains), thus decreasing the total magnetic energy. The former strongly (exponentially) depends on the spin-spin distance r while the latter depends on this distance as r^{-3}. In metallic iron (high spin density, about 0.2 spin Å^{-3}), domains are small (75 Å in size); in Fe_3O_4, the spin density is 0.05 spin Å^{-3} and the domain size is 300 Å. In purely organic ferromagnets, the spin density is very low (about 10^{-3} spin Å^{-3}) and both the exchange and dipole energies are therefore low; the domain size is larger than 100 nm, and the domain structure is observed only at very low temperatures (1—5 K). Molecular magnets with the domain sizes of the order of a few tens of nanometers occupy an intermediate position.

An internationally recognized leader in research on molecular ferromagnets is the International Tomography Center (ITC) of the Siberian Branch of the Russian Academy of Sciences headed by R. Z. Sagdeev and V. I. Ovcharenko. Researchers from the ITC synthesized a large number of novel ferromagnets based on high-spin molecular complexes with spin molecules as ligands. Some of them exhibit unique properties, *viz.*, being paramagnets at room temperature, they become ferromagnets on lowering the temperature, and then behave as antiferromagnets at even lower temperatures.[5,11,12]

Single-molecule magnets

Single high-spin molecules become particularly important as nanomagnets. They can be synthesized by classical chemistry methods, isolated, and purified as individual chemical substances. As chemical "cloning" products, they have absolutely identical sizes and structures. Each high-spin molecule is a point 0D nanomagnet and it exhibits the properties of a genuine magnet including spontaneous magnetization, magnetization anisotropy and hysteresis, internal domain structure, and dynamic hysteresis (frequency dependence of magnetization in alternating fields).

As a rule, these high-spin molecules contain tens (sometimes, hundreds) unpaired electrons which usually "reside" on transition-metal or rare-earth metal atoms concentrated at the center of the molecule and constituting its magnetic core. The core is surrounded by a diamagnetic shell comprised of organic ligands that "switch off" intermolecular exchange interaction between electrons and make the core magnetically insulated.[13]

The source of magnetism in these molecules is exchange interaction of electrons and dipole interaction of electron spins inside molecules. The constants of exchange interaction between different unpaired electrons inside a molecule usually have different values and signs. If the exchange interaction constant is positive, some electron spins are arranged parallel to one another (ferromagnetically). For other electrons, the exchange interaction constant is negative and their spins are aligned antiparallel to one another (antiferromagnetically). For this reason, the total spin of such molecules is as a rule smaller than the maximum value and their magnetic moment is much smaller than that expected for the maximum spin value. For instance, the total number of unpaired electrons in a single-molecule magnet with a $Mn_{30}O_{24}$ magnetic core is 143, but the spin of the molecule is only 5. Unlike macroscopic ferromagnets, nanodomains in single-molecule magnets change the magnetization direction by the tunneling mechanism. Because of this, quantum hysteresis loops in these molecules are "stepwise" in character.

If the constant D of magnetic dipole interaction between spins in a molecule is negative ($D < 0$), all spins divide into two ensembles with spin projections $M_s = \pm S$ separated by a barrier equal to DS^2. The magnetization of each ensemble is detected at a very low temperature called the blocking temperature T_b (usually, $3 < T_b < 5$ K). Above T_b, the magnetization relaxes and is averaged over both ensembles.

The main problem in chemistry of single-molecule magnets is to increase T_b to 50—100 K. The idea is as follows. The introduction of orbitally degenerate magnetic centers into a spin molecule causes the onset of strongly anisotropic exchange interactions which produce a high magnetic anisotropy of the molecule.**14—16** In this way, the T_b value can be significantly increased. Orbitally degenerate 4d- and 5d-complexes characterized by high exchange anisotropy and strong exchange interactions are the most promising in this respect. Examples are provided by pentagonal bipyramidal heptacyanide d^5-complexes $[Mo^{III}(CN)_7]^{4-}$ and $[Re^{IV}(CN)_7]^{3-}$ and by octahedral low-spin d^5-complexes $[Ru^{III}(CN)_6]^{3-}$ and $[Os^{III}(CN)_6]^{3-}$. Spin clusters formed by these complexes with 3d-ions (Cr^{3+}, Mn^{2+}) are characterized by increased blocking temperatures lying in the range 30—50 K. This is the direction taken by chemistry of single-molecule magnets.

Single-molecule magnets are very attractive as components of high-density magnetic memory devices and as hardware components for quantum computing and spintronics. Hundreds single-molecule magnets are available at the moment; almost all of them exhibit pure spin magnetism. When synthesizing such systems, one should keep in mind that there is no need to strive for a large number of unpaired electrons in a molecule, because, eventually, one almost always has $S < N/2$.

References

1. H. M. McConnell, *J. Chem. Phys.*, 1963, **39**, 1910.
2. A. L. Buchachenko, *Usp. Khim.*, 1990, **59**, 529 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1990, **59**].
3. A. L. Buchachenko, *Mol. Cryst. Liq. Cryst.*, 1989, **129**, 314.
4. A. L. Buchachenko, *Zh. Fiz Khim.*, 2009, **83**, 1637 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2009, **83**].
5. V. I. Ovcharenko, R. Z. Sagdeev, *Usp. Khim.*, 1999, **68**, 381 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1999, **68**].
6. A. F. Shestakov, A. L. Buchachenko, *Dokl. Akad. Nauk SSSR*, 1990, **310**, 407 [*Dokl. Chem.* (*Engl. Transl.*), 1990].
7. *Molecular Magnetism*, Eds K. Itoh, M. Kinoshita, Kodansha, Tokyo, 2000.
8. O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
9. M. Mito, T. Kawae, M. Hitaka, *Chem. Phys. Lett.*, 2001, **338**, 69.
10. A. Sundaresan, C. N. R. Rao, *Nano Today*, 2009, **4**, 96.
11. V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, R. Z. Sagdeev, *Zh. Struktur. Khim.*, 2002 **43**, 163 [*J. Struct. Chem.* (*Engl. Transl.*), 2002, **43**].
12. V. I. Ovcharenko, E. V. Gorelik, S. V. Fokin, R. Z. Sagdeev, *J. Am. Chem. Soc.*, 2007, **129**, 10512.
13. A. L. Buchachenko, *Usp. Khim.*, 2006, **75**, 3 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2006, **75**].
14. V. S. Mironov, *Dokl. Akad. Nauk*, 2006, **408**, 348 [*Dokl. Chem.* (*Engl. Transl.*), 2006].
15. V. S. Mironov, *Dokl. Akad. Nauk*, 2006, **408**, 130 [*Dokl. Chem.* (*Engl. Transl.*), 2006].
16. V. S. Mironov, L. F. Chibotaru, A. Ceulemans, *Phys. Rev.*, 2003, **B67**, 014424.

Received April 15, 2011