The Chemistry of Magnets

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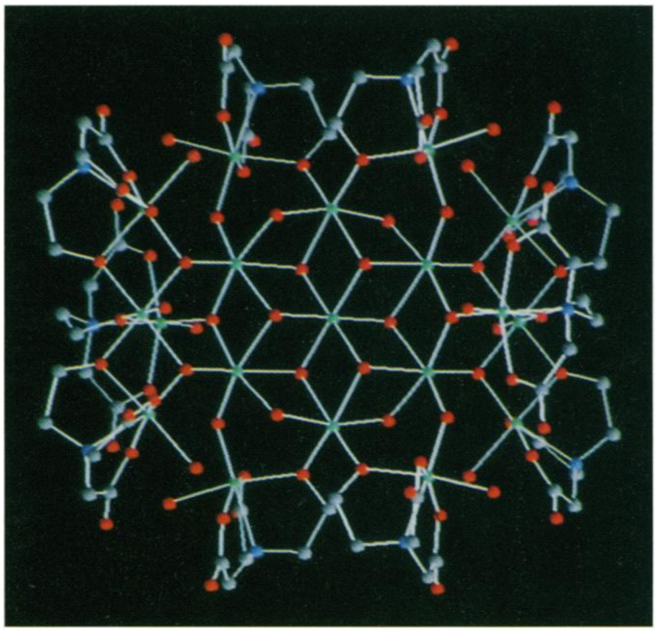
Magnetism and chemistry have had an up and down history together. From very early times, chemists thought that useful information about the bonds between atoms in molecules and solids could be derived from measurements of magnetic susceptibility. Faraday spent much time hanging samples of extremely diverse materials between the pole pieces of an electromagnet that he himself had made to detect differences of behavior between, as he put it, "a piece of wood, or beef, or apple obedient to or repelled by a magnet."

More recently, and more quantitatively, Pauling's seminal work of the 1930s on *The Nature of the Chemical Bond* (*2*) contained a lengthy section on "The Magnetic Criterion for Bond Type," and in the 1950s, the advent of ligand field theory made the measurement of bulk magnetic susceptibility respectable as a way of learning about metal-ligand covalency and the symmetry of coordination around transition metal ions. However, despite the fact that bulk susceptibility measures just that—the reaction of the whole sample to an applied field—until recently, only a small minority of chemists have interested themselves in the effects of interaction between the neighboring metal ions in an extended lattice.



Trapping iron. One approach to the synthesis of molecular magnets is to create hydroxo(oxo)polyiron complexes, as shown here. Iron atoms, green; oxygen, red. [Reprinted from (*4*) with permission] Stumpf *et al.* (*3*) take another approach, namely the synthesis of a three-dimensional interlocking network of manganese and copper spin carriers.

Meanwhile, the world of "real" magnets, dominated by physics and materials science, goes on, as it has since the time of Faraday, in its preoccupation with metals, objects that are opaque, shiny, and go clang when they hit the floor. These materials do not overlap much with the kind of compounds that chemists make in their flasks and beakers, you may think. Furthermore, the information-storage industry (which embraces audio tapes as well as more sophisticated hard disks) relies heavily on transition metal oxides, whether simple binary ones like γ-Fe_2O_3 and CrO_2 or complex solid solutions based on the garnet or ferrite structures. Still, all the while, a small dedicated band of chemists has been trying to synthesize substances that have a bulk spontaneous magnetization.

The report by Stumpf *et al.* on page 447 is an excellent example of the genre (*3*). The authors discuss their synthesis of a material, formed from perpendicular, interlocking graphite-like networks of spin centers, that exhibits bulk magnetization below 22.5 K. Given that so many conventional magnetic materials are available with Curie temperatures (T_c's) far above room temperature, not to mention high coercive and remanent fields, it is worth asking why so much effort is being devoted to the synthesis of substances with Curie temperatures of only 22.5 K.

One reason, by no means to be ignored, is the sheer novelty of this approach to cooperative magnetism. Making new molecular architectures, tailored to have a specific property, is very much a task for chemists. Another important feature characterizing such nonconducting magnets is their transparency, certainly not something normally associated with spontaneous magnetization. For example, magnets whose optical spectra consist of discrete absorption bands may change their transparency or birefringence quite dramatically when long-range spin correlations build up as a function of temperature or applied field. Should transparent materials be synthesized with spontaneous magnetization close to 300 K, applications in data storage and telecommunications would surely follow.

There are several other features of potential practical import that distinguish magnetic materials based on molecules from their analogs consisting of continuous ionic or metallic lattices. Synthetic methods are, of course, quite different, based on the traditional methods espoused by coordination or organometallic chemists, such as crystallization from solution close to room temperature. Consequently, thin films might be deposited with methods, such as solvent evaporation or spin-coating, that are familiar from polymer science.

Could magnetization be associated with other properties found exclusively in molecular assemblies such as mesomorphism? For the time being, we do not know. A variant on molecular-based magnets is to enrobe clusters of inorganic material with an organic coating, on the way to mimicking biological objects like ferritin or the small particles of magnetic oxide used by bacteria (or even pigeons) as a means of navigation. The figure shows such a recent system containing 19 exchange-coupled Fe^{3+} centers (*4*).

If all of the above are taken as good and sufficient reasons to try to make molecular-based magnets, how should the job be tackled? The first point is that to make magnetic materials that are not metallic conductors, one can concentrate on designing lattices in which the magnetic exchange interactions that order the localized moments are principally between nearest neighbors. Sometimes it may be necessary to think about next-nearest neighbors and even, quite exceptionally, third-nearest neighbors. Long-range exchange, of the RKKY type, for instance, which involves conduction electrons, does not have to be considered. From that point, the options are easily defined: Clearly, one can try to engineer near-neighbor ferromagnetic exchange, but exploiting ferromagnetism is also an attractive possibility. In the latter, the exchange interaction between dissimilar ions is antiferromagnetic, but because they have different moments, there is a net resultant moment. A third option is to make lattices containing antiferromagnetic near-neighbor interactions of sufficiently low symmetry that the moments are not exactly antiparallel but make a small angle to one another, called canting. Then there remains a small, uncompensated component giving what is called weak ferromagnetism.

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All of these strategies have been tried, and over the last 10 to 15 years, all have led to insulating magnetic compounds. The rules relating the symmetry and occupation of orbitals on neighboring centers to the sign of the exchange interaction have been known for nearly 40 years under the names of Kanamori and Goodenough (*5*), so that (for example) combinations of octahedrally coordinated Cr(III) and Ni(II) linked through a bridging ligand are invariably ferromagnetically coupled.

Simpler predecessors of the elaborate networks in the compound reported on page 447 (*3*) were built from metal complexes, with ambidentate ligands, that form bimetallic chain polymers (*6*). The recipe is straightforward: make a complex of metal A with a ligand that is capable of binding a second metal B on its back side. The polymers have to be built into three-dimensional arrays in such a way that interactions between the nearest ions on adjacent chains allow the spins to add and not subtract, a tricky problem to which much experimental imagination has been devoted. Transmission of the interaction through bridging organic molecules has also been explored by the construction of discrete dimers, blocking off further polymerization with capping ligands. Typical bridging ligands are oxalate, dithiooxalate, and oxamate. Very large intramolecular ferromagnetic exchange arises in dimers when a transition metal ion with a single *d* electron is combined with one containing a single hole in an otherwise filled *d* shell, specifically VO^{2+} and Cu^{2+}. That is because the single electron centered on the V is in an orbital of *xy* type, whereas the hole on the Cu is in an x^2-y^2 orbital.

This illustrates an important general recipe for ferromagnetic exchange, namely that the orbitals bearing the moments must be orthogonal. Unfortunately, except in rather specialized cases, it has not proved very easy to make networks obeying this principle, though one method that I used some 10 to 15 years ago exploits the Jahn-Teller effect as a way of spatially ordering the moments (*7*). That is why ferrimagnetism, based on two different antiferromagnetically coupled sublattices, is more commonly used. The biggest possible saturation magnetization occurs when the two metal ions have as large a difference as possible in spin quantum number. Among transition metal ions, that condition leads one to combine Cu^{2+} (S = 1/2) with Mn^{2+} (S = 5/2). Pursuing the same line of thought further, several groups considered combinations of 4*f* and 3*d* ions, the former being often Gd^{3+} (S = 7/2) (*8*). The Achilles heel of that approach, however, is the small exchange constant resulting from small overlap between well-shielded *f* and 3*d* orbitals.

Although they are prepared from molecular precursors, the magnets discussed so far are not, strictly speaking, molecular themselves but are really polymeric. Examples of spontaneous magnetization among truly molecular solids—that is, ones in which the intermolecular contacts are all at van der Waals distances—are extremely few and far between. To be precise, just one compound of this type has been uncovered and thoroughly investigated: $\{Fe[C_5(CH_3)_5]_2\}$(TCNE) (tetracyanoethylene), made by Miller and Epstein in the late 1980s (*9*).

This material has a chain structure based on alternating organometallic cations and TCNE anions that come together plane-to-plane. Its T_c is 4.8 K, and it has a relatively large coercive field of 1000 G. The mechanism of spin alignment is almost certainly different than that in coordination polymers, in which superexchange provides the answer. The most plausible explanation for the ferromagnetic sign was first proposed back in the 1960s by McConnell (*10*). He suggested that if one of two alternating molecular ions forming a chain had two molecular orbitals of similar energy, the transfer of an electron from one ion to the other would stabilize the arrangement with the maximum number of unpaired electrons. The conditions for forming such an arrangement must be extraordinarily demanding because Miller and his colleagues synthesized some dozens of salts closely related to $\{Fe[C_5(CH_3)_5]_2\}$(TCNE) without finding any others that were ferromagnets.

Apart from transition metal ions, another source of degenerate orbitals to test the McConnell mechanism would be a p system of an aromatic organic molecule with high symmetry. But unpaired *p* electrons in organic chemistry usually go under the name of free radicals because they are chemically very reactive. Therefore, the first thing to do when trying to make purely organic magnets is to shield the unpaired electrons from the outside world with bulky substituents. In that way, high-spin molecules have been prepared, although this is only the start: The molecules must interact ferromagnetically with each other to make a bulk material. In fact, the first bulk ferromagnet containing only elements of the first short row of the periodic table is just about 2 years old (*11*), although a small family of related compounds is being built up quite rapidly. The molecules in question are nitronyl nitroxides, each of which contains two NO groups connected by a single =CH–, carrying a single unpaired electron. Variation of the substituents makes possible some crystal structure engineering leading to correlations between magnetic properties and molecular packing. The bad news is that the Curie temperatures are extremely low [the current record is only 1.48 K (*12*)].

There is a long way to go before we shall see molecular-based magnets turning up in audio tapes or storage disks. On the other hand, the efforts so far have turned up a lot of new chemistry and brought synthetic chemists into close contact with physics and materials science. In Europe, the latter is being helped through funding by the European Community under its Human Capital and Mobility Programme, and a first workshop took place in Italy at the beginning of the month. Momentum in that part of the world is being matched in Japan and the United States, showing that chemists are becoming enthusiastic about magnetism again.

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